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The purpose of this review is threefold: first, to examine the effects of temperature on the physical and chemical properties of natural waters (specifically waters of interest to the continental United States); second, to discuss some of the influences of the chemical changes - effected by temperature changes - on the suitability of these waters to support life; and finally, to delineate some of the effects and the underlying mechanisms of temperature changes on the cell chemistry of the aquatic biota - that is, a thermochemical perspective of the aquatic biology under possible heat stress. Portions of this document are not fully legible.

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Ions,
Dissociation,
Heat of vaporization,
Specific heat,
Thermal conductivity,
Viscosity,
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PB 257 612

ASPECTS OF THE RELATIONSHIP BETWEEN TEMPERATURE AND AQUATIC CHEMISTRY

by

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May 1973

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PART I

SECTION I: INTRODUCTION

I. INTRODUCTION

A. Objectives

The purpose of this review is threefold: first, to examine the effects of temperature on the physical and chemical properties of natural waters (specifically waters of interest to the continental United States); second, to discuss some of the influences of the chemical changes - effected by temperature changes - on the suitability of these waters to support life; and finally, to delineate some of the effects and the underlying mechanisms of temperature changes on the cell chemistry of the aquatic biota - that is, a thermochemical perspective of the aquatic biology under possible heat stress.

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B. Biotic Responses to Temperature

In Part I, Section I,C, is discussed the effects of temperature changes on model systems - serving as approximations to real, natural water systems - in terms of both physical properties and a number of chemical equilibria and rate processes. In principle, since attention is restricted to the temperature range from approximately 0°C to approximately 40°C,* the problem is essentially "straightforward" - at least to within the approximations afforded by the model systems chosen to represent the actual natural waters. Standard physical chemistry accounts reasonably well for temperature effects on dilute but aqueous solutions of electrolytes. The second task, to determine the effects of the chemical changes (effected by temperature variations) on the biota is far more complex. For this reason, the second task will be reduced to considerations of two different, distinct problems. First, it will be demonstrated that the chemical changes effected by small temperature changes are probably without any dramatic influence on the overall ecology of a local region. Obviously, any temperature change will change the ecology. This statement is almost axiomatic. However, while nearly obviously true, it is also likely, as will be evidenced, that the changes are relatively minor, though likely readily detectable. Whether these changes will be beneficial or detrimental is beyond the realm of this investigation (and beyond the ability of the present investigator to determine). In the second major aspect of this study, some specific influences of aquatic temperature changes directly on various organisms will be considered in some detail.

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*Thus excluding such unique environments as hot springs.

We conclude this brief introduction by stressing one of the main results of the investigation: the effects of temperature on the aquatic chemistry are probably of minimal consequences, at least for the ecology for small temperature changes, in "safe temperature intervals" (the meaning of the expression "safe temperature intervals" to be discussed at length below, in Section 2·IV·V). However, near certain "critical temperature ranges" (also to be explicitly defined and discussed in a subsequent section), dramatic and generally highly deleterious ecological effects can be expected. These latter changes are brought about at characteristic, narrow temperature intervals, apparently as the result of chemical changes internal to the organism (rather than due to the relatively modest chemical changes in the chemistry of the external, bulk environment).

C. Modeling of Environmental, Aquatic Systems

Morgan (1967) has discussed the "applications and limitations of chemical thermodynamics in natural water systems". This study delineates some conceptual models by which a "real" situation may be approximated by generalized models to which at least in principle, thermodynamics is applicable. The two systems primarily advocated by Morgan allow, respectively, for a thermodynamic description of an essentially closed system, and for a chemical dynamics description, allowing for material exchanges (inputs and outflows) and energy exchanges. The natural extension of this system would be to the inclusion of biological phenomena. Figure I-01 and Figure I-02 show, respectively, Morgan's two systems. Unfortunately, Morgan mentions only briefly the principle by which a connection can be made between the thermodynamic description of a chemical reaction system and the actual kinetics. The link is provided via the general field of irreversible chemical thermodynamics. Formally, the simplest expression is the formula for the rate of internal energy production, dS_i/dt. This rate of entropy production is related to the overall velocity of the chemical reaction, as seen in equation (1) .

$$\frac{dS_i}{dt} = \frac{A}{T} \cdot \frac{d\xi}{dt} = \frac{A}{T} \cdot v \qquad (1)$$

Here $v = d\xi/dt$ is the velocity of the chemical reaction. dS_i/dt is the rate of internal energy production. ξ_i is the degree of advancement of the reaction. In Equation (1), A is the affinity ($= -\Sigma \nu_i \mu_i$).

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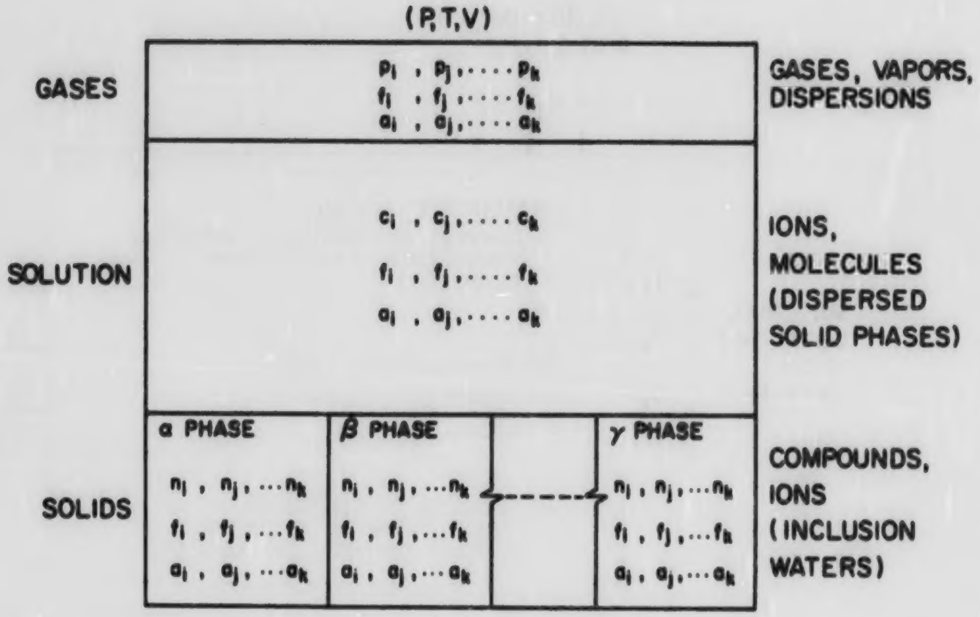
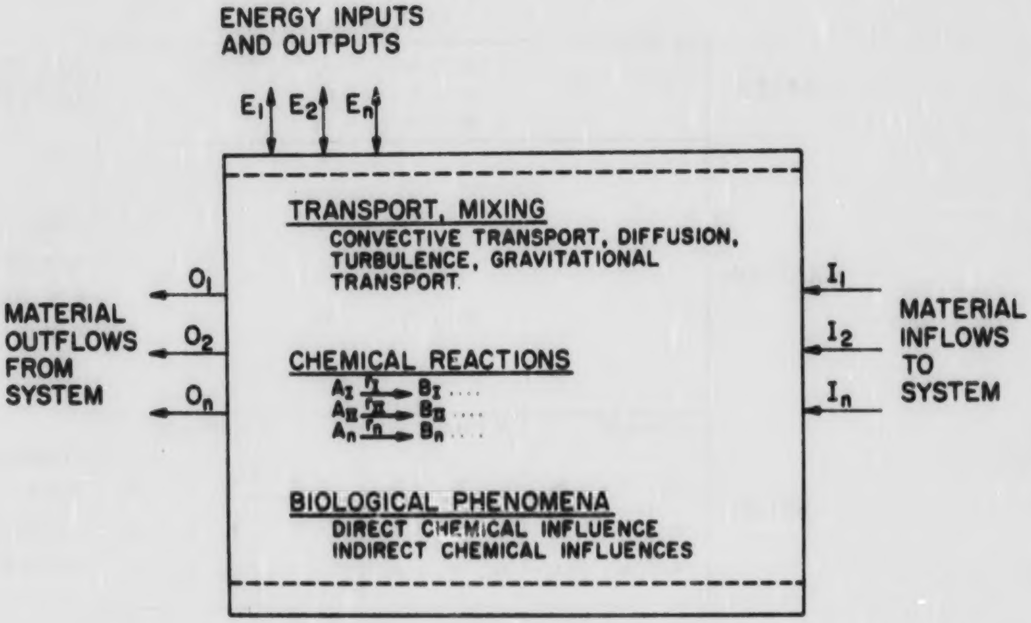

(P,T,V)
GASES
p_i , p_j ,.... p_k
f_i , f_j ,.... f_k
a_i , a_j ,.... a_k
GASES, VAPORS, DISPERSIONS
SOLUTION
c_i , c_j ,.... c_k
f_i , f_j ,.... f_k
a_i , a_j ,.... a_k
IONS, MOLECULES (DISPERSED SOLID PHASES)
SOLIDS
α PHASE
β PHASE
γ PHASE
n_i , n_j ,... n_k
f_i , f_j ,... f_k
a_i , a_j ,... a_k
COMPOUNDS, IONS (INCLUSION WATERS)

A Generalized Model for the Thermodynamic Description of Natural Water Systems (Morgan, in Stumm, 1967, page 9).

Figure 1-01


ENERGY INPUTS AND OUTPUTS
E1
E2
En
TRANSPORT, MIXING
CONVECTIVE TRANSPORT, DIFFUSION, TURBULENCE, GRAVITATIONAL TRANSPORT
CHEMICAL REACTIONS
AI rI BI ....
AII rII BII ....
An rn Bn ....
BIOLOGICAL PHENOMENA
DIRECT CHEMICAL INFLUENCE
INDIRECT CHEMICAL INFLUENCES
MATERIAL OUTFLOWS FROM SYSTEM
O1
O2
On
MATERIAL INFLOWS TO SYSTEM
I1
I2
In

Generalized Model for a Chemical, Dynamic Description of Natural Water Systems with Material and Energy Exchanges Across Boundaries. (Morgan, in Stumm, 1967, page 14).

Figure I-02

In the present review, it is not possible to take into account the effects of a temperature change on an open, dynamic model system. The theory for this is only being developed right now (see, for instance, Glansdorff and Prigogine, "Thermodynamic Theory of Structure, Stabilility and Fluctuations", 1971). The problem is complicated in the sense that the actual natural water system may be far from equilibrium initially (and even further from equilibrium after a change in the temperature has been imposed via a man-made energy exchange). Thus, the obvious changes - such as enhanced vapor pressure and rate of evaporation - will obviate the possibility of obtaining accurate answers by considering merely closed equilibrium thermodynamic systems.

For an open system the stationary state is one characterized by an entropy production (assuming fixed affinities or concentrations in the environment). The stationary state has been described by Prigogine (1961) as the state of minimum entropy production; in other words, the least free energy dissipation.

In his treatment of open and dynamic model systems, Morgan calls attention to the general equation for a system in which the concentration of any constituent (i) is a function of space and time.

$$\frac{\partial C_i}{\partial t} + u\frac{\partial C_i}{\partial x} + \rho\frac{\partial C_i}{\partial y} + w\frac{\partial C_i}{\partial z} = \frac{\partial}{\partial x}\left(D_x\frac{\partial C_i}{\partial x}\right) + \frac{\partial}{\partial y}\left(D_y\frac{\partial C_i}{\partial y}\right) + \frac{\partial}{\partial z}\left(D_z\frac{\partial C_i}{\partial z}\right) + r_{i,n} \qquad (2)$$

Where terms of the form $a \cdot \frac{\partial C_i}{\partial P}$ are the advective or convective terms and expressions of the form $\frac{\partial}{\partial p} (D_p \cdot \frac{\partial C_i}{\partial p})$ are terms related to diffusion or turbulent transport (depending on the hydrodynamic situation). $r_{i,n}$ is the rate of formation or disappearance of the constituent $\underline{i}$ by any process (N) in the vicinity of point of interest. It is seen that the equation is composed of advective or convective terms, diffusion or turbulent transport terms and rates of disappearance or formation of a constituent.

In the present review, attention is concentrated on two types of systems: idealized model systems, consisting of closed equilibrium thermodynamic systems for which changes in parameters and properties are calculated (either from theory or based on experimental data) for properties as a function of temperature. The second facet to be dealt with are temperature changes in a non-equilibrium (and sometimes non-steady) state, such as living systems; here the temperature effects are directly on the functioning of the cellular organism. Kinetic phenomena, per se, will receive only relatively little attention. The treatment primarily deals, in this case, with the kinetics of processes in colloidal systems, specifically rate variations as a function of temperature.

In the "realistic" model systems - which is, at best, a first order approximation - it is specifically assumed that one needs to be concerned only with the effects of temperature on a constant chemical environment as opposed to a real system in which large-scale random changes may occur. Thus, the treatment does not allow for the effects of temperature, on an otherwise "steady-state" system, suddenly subject to dumping of major or minor chemical constituents into the system (such as may occur as the result of a heavy rainfall, unexpected runoff from fertilized water sheds, or variable inputs from private or municipal water treatment plants which may be operating subject to large fluctuations).

Please note, unless specifically stated otherwise, all measurements are in cgs units. Also note particularly the consistent use of temperatures in degrees Celsius ("Centigrade"); or, where appropriate, degrees Kelvin. Where temperatures are discussed which are derived from quotes in the literature - in all but direct quotes - the temperatures have been converted to degrees Celsius. Generally, the conversion is at least to within the nearest degree Celsius.

Finally, it should be observed that the aim of the present review is twofold: estimating temperature effects on the intrinsic ("equilibrium") chemistry - i.e., concentration, ion activities and general properties. The second major aspect is the effects of temperature on the organisms as effected through the internal chemical changes. The connection between the chemical changes effected by temperature and the suitability of these natural waters to support life are thus deliberately separated into two distinctly differing aspects. What is left out of consideration, then, is the "feedback"; the effects which the temperature exerts on the organisms and which, in turn, alters the chemistry - often dramatically - (for instance, through metabolic use of oxygen, exchange of ions, etc.).

In Section II, thermal effects on physico-chemical properties of water and selected electrolyte solutions are examined in some detail. Attention is restricted essentially to the temperature range from 0 to 40° - the principal limits for naturally occurring aquatic environments. It is obvious that the properties of both pure water and aqueous solutions are functions of temperature. These temperature dependencies have, in many cases, been determined with great accuracy and extreme precision. In the present context, however, only essential features of these temperature variations have been considered for practical reasons. Where available, data are reported, over the temperature range from 0 to (at least) 40° in sufficiently small increments to allow reasonably accurate interpolations to be made.

The main objective of the first part of this study may be stated simply as the determination of the changes in the chemistry of natural waters effected by a reasonable thermal input into a localized body of water. Somewhat arbitrarily, for sake of discussion, a maximum of 5 or 10°C temperature increase has been adopted in this analysis. In other words, if the ambient temperature of the water body in question is 15° on the average, a maximum temperature rise of 10° (to 25°C) will be considered. The question is: what effects does such a temperature increase have on the chemistry and, in turn, on the population of organisms in this body of water? In the first part of the study, the effect is treated, in a sense, as an abstraction. In other words, the emphasis is on the change in the suitability of the water as a medium for sustaining life due to the resulting changes in the chemistry. What is excluded, then, in this discussion is the intrinsic effects of the temperature on the organisms internally which will ultimately be reflected in the chemistry of the environment.

The above limitation is, in a sense, highly unfortunate from the point of view of the ecology. For this reason, the second part of this review deals specifically with some selected (but not general) aspects of temperature effects on cellular organisms. However, the simplification proposed may be justified pragmatically in terms of the enormous complexity of the natural system - requiring some simplifications to be made - and in part by the conclusion which results from this study; namely, that the relatively minor changes in chemical composition, which are brought about by a 10° temperature change, are not likely to affect significantly the overall ecology. Thus, further studies of temperature changes on aquatic ecology may be better served by increased attention to the changes in the cellular chemistry, rather than in excessive efforts to monitor in detail the overall "bulk" chemistry of the natural waters.

PART I

SECTION II: PHYSICO-CHEMICAL CHANGES - THERMAL EFFECTS

A. General Observations

In classical physical chemistry, the effect of temperature on equilibria and on rate processes are traditionally represented by van't Hoff plots and Arrhenius plots, respectively. In either case, the logarithm of the quantity in question is plotted as a function of reciprocal absolute temperature. Traditional interpretations (subject to many limitations) are usually restricted to straight line segments of such curves. As an example, for solubility data, the slope gives the heat of solution; for rate processes, the slope is the Arrhenius energy of activation. Enumerable detailed treatments of these quantities can be found in standard texts on physical chemistry.

In Table I is shown a general survey of some characteristic physical properties of water as a function of temperature. More detailed information about these variables are fuond in Section II-B.

TABLE I

GENERAL SURVEY:

PHYSICAL PROPERTIES OF WATER AT ATMOSPHERIC PRESSURE

t_{68}, °C	Vapor Pressure bar	Density, kg m^{-3}	Isothermal compressibility, bar^{-1}	Isobaric specific heat, Jg^{-1}	Temp. °C	Dielectric constant	Viscosity centipoise
0	0.00611	999.840	50.866	4.2174	0	$87{\cdot}74_0$	1·787
5	0.00872	999.964	49.170	4.2019	5	$85{\cdot}76_3$	1·516
10	0.01228	999.700	47.810	4.1919	10	$83{\cdot}83_2$	1·306
15	0.01705	999.100	46.735	4.1855	15	$81{\cdot}94_5$	1·138
20	0.02338	998.204	45.894	4.1816	20	$80{\cdot}10_3$	1·002
25	0.03169	997.045	45.249	4.1793	25	$78{\cdot}30_3$	0·8903
30	0.04245	995.648	44.773	4.1782	30	$76{\cdot}54_6$	0·7975
35	0.05627	994.032	44.443	4.1779	35	$74{\cdot}82_3$	0·7194
40	0.07382	992.215	44.243	4.1783	40	$73{\cdot}15_1$	0·6531
45	0.09591	990.212	44.158	4.1792	45	$71{\cdot}51_1$	0·5963
50	0.12346	988.033	44.179	4.1804	50	$69{\cdot}91_0$	0·5467
55	0.15754	985.691	44.297	4.1821	55	$68{\cdot}34_4$	0·5044
60	0.19936	983.193	44.504	4.1841	60	$66{\cdot}81_3$	0·4666
65	0.25027	980.548	44.797	4.1865	65	$68{\cdot}31_9$	$0{\cdot}434_2$
70	0.31181	977.761	45.171	4.1893	70	$63{\cdot}85_5$	$0{\cdot}404_9$

B. Densities, Specific Volumes of Water and Seawater

Extensive discussion of the density of water can be found both in Dorsey (1940) and in Gmelin (loco cit., page 1317-1323). Table I-02 shows the tabulated values reported in Gmelin (page 1322-1323) based on the recalculated data of Chappui, according to Tilton and Taylor (1937).

t	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0°	0.9998676	0.9998743	0.9998808	0.9998871	0.9998933	0.9998993	0.9999051	0.9999107	0.9999161	0.9999214
1°	0.9999265	0.9999314	0.9999362	0.9999407	0.9999451	0.9999493	0.9999534	0.9999573	0.9999610	0.9999645
2°	0.9999678	0.9999710	0.9999740	0.9999769	0.9999796	0.9999821	0.9999844	0.9999866	0.9999886	0.9999905
3°	0.9999922	0.9999937	0.9999950	0.9999962	0.9999972	0.9999981	0.9999988	0.9999993	0.9999997	0.9999999
4°	1.0000000	0.9999999	0.9999996	0.9999992	0.9999986	0.9999979	0.9999970	0.9999960	0.9999948	0.9999934
5°	0.9999919	0.9999902	0.9999884	0.9999864	0.9999843	0.9999820	0.9999796	0.9999770	0.9999743	0.9999715
6°	0.9999683	0.9999651	0.9999618	0.9999583	0.9999546	0.9999508	0.9999469	0.9999428	0.9999386	0.9999342
7°	0.9999297	0.9999250	0.9999202	0.9999153	0.9999102	0.9999049	0.9998995	0.9998940	0.9998883	0.9998825
8°	0.9998765	0.9998704	0.9998642	0.9998578	0.9998513	0.9998446	0.9998378	0.9998309	0.9998238	0.9998166
9°	0.9998092	0.9998017	0.9997941	0.9997863	0.9997784	0.9997704	0.9997622	0.9997539	0.9997454	0.9997368
10°	0.9997281	0.9997193	0.9997103	0.9997012	0.9996919	0.9996825	0.9996730	0.9996634	0.9996536	0.9996437
11°	0.9996336	0.9996234	0.9996131	0.9996027	0.9995922	0.9995815	0.9995706	0.9995597	0.9995486	0.9995374
12°	0.9995261	0.9995146	0.9995030	0.9994913	0.9994795	0.9994675	0.9994554	0.9994432	0.9994309	0.9994184
13°	0.9994059	0.9993932	0.9993805	0.9993674	0.9993543	0.9993411	0.9993278	0.9993143	0.9993007	0.9992870
14°	0.9992732	0.9992593	0.9992453	0.9992311	0.9992168	0.9992024	0.9991879	0.9991732	0.9991584	0.9991436
15°	0.9991286	0.9991134	0.9990982	0.9990828	0.9990674	0.9990518	0.9990360	0.9990202	0.9990043	0.9989882
16°	0.9989721	0.9989558	0.9989394	0.9989229	0.9989062	0.9988895	0.9988726	0.9988557	0.9988386	0.9988214
17°	0.9988041	0.9987867	0.9987691	0.9987515	0.9987337	0.9987158	0.9986979	0.9986798	0.9986616	0.9986433
18°	0.9986248	0.9986063	0.9985877	0.9985689	0.9985501	0.9985311	0.9985120	0.9984928	0.9984735	0.9984541
19°	0.9984346	0.9984150	0.9983953	0.9983754	0.9983555	0.9983355	0.9983153	0.9982950	0.9982747	0.9982542
20°	0.9982336	0.9982130	0.9981922	0.9981713	0.9981503	0.9981292	0.9981080	0.9980867	0.9980653	0.9980438
21°	0.9980221	0.9980004	0.9979786	0.9979567	0.9979346	0.9979125	0.9978903	0.9978679	0.9978455	0.9978230
22°	0.9978003	0.9977776	0.9977547	0.9977318	0.9977088	0.9976856	0.9976624	0.9976390	0.9976156	0.9975921
23°	0.9975684	0.9975447	0.9975208	0.9974969	0.9974729	0.9974487	0.9974245	0.9974002	0.9973758	0.9973512
24°	0.9973266	0.9973019	0.9972771	0.9972522	0.9972272	0.9972021	0.9971769	0.9971516	0.9971262	0.9971007
25°	0.9970751	0.9970494	0.9970237	0.9969978	0.9969718	0.9969458	0.9969196	0.9968934	0.9968671	0.9968406
26°	0.9968141	0.9967875	0.9967608	0.9967340	0.9967071	0.9966801	0.9966530	0.9966258	0.9965986	0.9965712
27°	0.9965437	0.9965162	0.9964886	0.9964608	0.9964330	0.9964051	0.9963771	0.9963490	0.9963208	0.9962926
28°	0.9962642	0.9962358	0.9962072	0.9961786	0.9961499	0.9961211	0.9960922	0.9960632	0.9960341	0.9960049
29°	0.9959757	0.9959463	0.9959169	0.9958874	0.9958578	0.9958281	0.9957983	0.9957684	0.9957384	0.9957084
30°	0.9956783	0.9956480	0.9956177	0.9955874	0.9955569	0.9955263	0.9954956	0.9954649	0.9954341	0.9954032
31°	0.9953722	0.9953411	0.9953099	0.9952787	0.9952473	0.9952159	0.9951844	0.9951528	0.9951211	0.9950894
32°	0.9950575	0.9950256	0.9949936	0.9949615	0.9949293	0.9948970	0.9948647	0.9948323	0.9947997	0.9947671

t	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
33°	0.9947344	0.9947016	0.9946688	0.9946358	0.9946028	0.9945698	0.9945366	0.9945033	0.9944700	0.9944365
34°	0.9944030	0.9943694	0.9943358	0.9943020	0.9942682	0.9942343	0.9942003	0.9941662	0.9941320	0.9940978
35°	0.9940635	0.9940291	0.9939946	0.9939600	0.9939254	0.9938907	0.9938559	0.9938210	0.9937860	0.9937510
36°	0.9937159	0.9936807	0.9936454	0.9936100	0.9935746	0.9935391	0.9935035	0.9934678	0.9934321	0.9933962
37°	0.9933604	0.9933244	0.9932883	0.9932522	0.9932160	0.9931797	0.9931433	0.9931068	0.9930703	0.9930337
38°	0.9929970	0.9929603	0.9929234	0.9928865	0.9928495	0.9928125	0.9927753	0.9927381	0.9927008	0.9926634
39°	0.9926260	0.9925884	0.9925508	0.9925132	0.9924754	0.9924376	0.9923997	0.9923617	0.9923236	0.9922855
40°	0.9922473	0.9922090	0.9921707	0.9921323	0.9920938	0.9920552	0.9920165	0.9919778	0.9919390	0.9919001
41°	0.9918612	0.9918221	0.9917830	0.9917439	0.9917046	0.9916653	0.9916259	0.9915864	0.9915469	0.9915073

Table I-02

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Table 1-03

Specific Volume $\bar{V}$ of Ordinary Water under Pressure*

P, kbar	t, °C								
	0	25	50	75	100	125	150	175	200
0.5	0.97666	0.98185	0.99135	1.00421	1.02008	1.03887	1.0607	1.0860	1.1149
1.0	0.95656	0.96344	0.97321	0.98552	1.00016	1.0171	1.0363	1.0578	1.0826
1.5	0.9385	0.9471	0.9572	0.9696	0.9839	0.9995	1.0174	1.0366	1.0588
2.0	0.9241	0.9341	0.9447	0.9561	0.9681	0.9822	0.9989	1.0166	1.0368
2.5	0.9117	0.9218	0.9321	0.9430	0.9544	0.9675	0.9824	0.9987	1.0172
3.0	0.9005	0.9106	0.9209	0.9317	0.9426	0.9550	0.9689	0.9839	1.0004
3.5	0.8901	0.9002	0.9105	0.9212	0.9320	0.9440	0.9572	0.9707	0.9860
4.0	0.8805	0.8906	0.9009	0.9114	0.9220	0.9338	0.9465	0.9595	0.9733
4.5	0.8715	0.8815	0.8918	0.9022	0.9128	0.9241	0.9361	0.9485	0.9617
5.0	0.8627	0.8727	0.8829	0.8933	0.9038	0.9148	0.9264	0.9385	0.9511
5.5	0.8551	0.8649	0.8749	0.8851	0.8952	0.9059	0.9171	0.9269	0.9410
6.0	0.8481	0.8577	0.8675	0.8773	0.8872	0.8976	0.9084	0.9199	0.9316
6.5	(0.8417)	0.8510	0.8605	0.8701	0.8798	0.8901	0.9004	0.9116	0.9229
7.0	—	0.8451	0.8543	0.8636	0.8730	0.8829	0.8929	0.9037	0.9147
7.5	—	0.8393	0.8483	0.8574	0.8666	0.8772	0.8871	0.8971	0.9071
8.0	—	0.8339	0.8427	0.8516	0.8606	0.8709	0.8805	0.8902	0.8999

Table I-04

VOLUME PROPERTIES OF ORDINARY WATER

G. S. KELL

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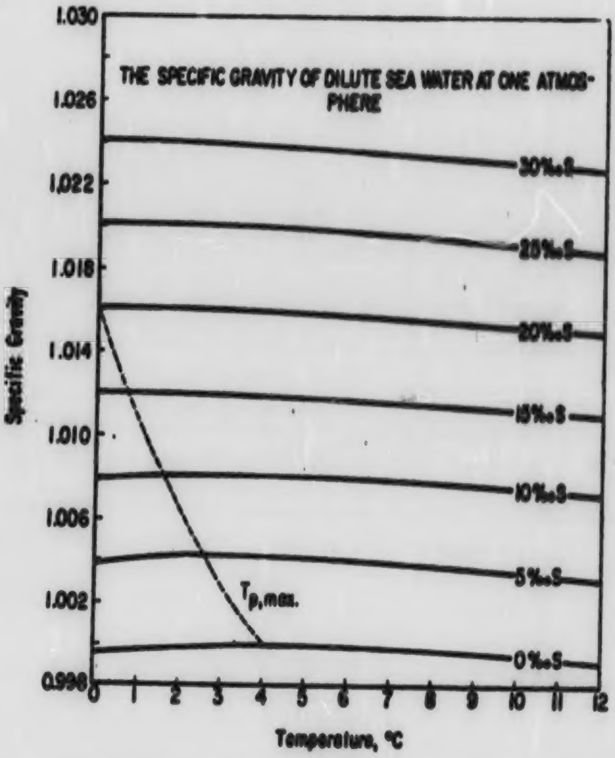
of Journal of Chemical and Engineering Data, 12, 67-68 (1967)

(Specific volume v, density ρ, thermal expansivity $\alpha = d \ln v/dt = -d \ln \rho/dt$, compressibility $\kappa = -d \ln v/dp = d \ln \rho/dp$)

t, °C.	v, Cc./G.	ρ, G./Ml.	$10^6\alpha$, Deg.$^{-1}$	$10^6\kappa$, Bar^{-1}
−20	1.00658	0.99349	−678.48	61.94
−18	1.00532	0.99474	−580.83	60.48
−16	1.00424	0.99581	−495.74	59.11
−14	1.00332	0.99672	−420.85	57.83
−12	1.00254	0.99749	−354.33	56.64
−10	1.001895	0.998137	−294.73	55.52
−9	1.001614	0.998417	−267.18	54.99
−8	1.001359	0.998671	−240.95	54.48
−7	1.001131	0.998899	−215.94	53.98
−6	1.000926	0.999102	−192.06	53.50
−5	1.000746	0.999283	−169.22	53.04
−4	1.000587	0.999441	−147.34	52.60
−3	1.000451	0.999578	−126.36	52.17
−2	1.000334	0.999694	−106.20	51.76
−1	1.000238	9.999790	−86.81	51.36
0	1.000160	0.999868	−68.14	50.98
1	1.000101	0.999927	−50.14	50.61
2	1.000060	0.999968	−32.77	50.26
3	1.000036	0.999992	−15.98	49.92
4	1.000028	1.000000	0.26	49.59
5	1.000036	0.999992	15.98	49.28
6	1.000060	0.999968	31.23	48.98
7	1.000098	0.999930	46.01	48.69
8	1.000151	0.999877	60.37	48.41
9	1.000219	0.999809	74.33	48.15
10	1.000300	0.999728	87.90	47.89
11	1.000395	0.999634	101.12	47.65
12	1.000502	0.999526	113.99	47.42
13	1.000623	0.999406	126.54	47.19
14	1.000755	0.999273	138.78	46.98
15	1.000900	0.999129	150.73	46.78
16	1.001057	0.998972	162.41	46.59
17	1.001225	0.998804	173.82	46.40
18	1.001405	0.998625	184.99	46.23
19	1.001596	0.998435	195.91	46.06
20	1.001797	0.998234	206.61	45.91
21	1.002010	0.998022	217.10	45.76
22	1.002232	0.997801	227.37	45.62
23	1.002465	0.997569	237.45	45.48
24	1.002708	0.997327	247.34	45.36
25	1.002961	0.997075	257.05	45.24
26	1.003224	0.996814	266.59	45.13
27	1.003496	0.996544	275.96	45.02
28	1.003778	0.996264	285.17	44.93
29	1.004069	0.995976	294.23	44.84
30	1.004369	0.995678	303.14	44.75
31	1.004678	0.995372	311.92	44.67
32	1.004995	0.995057	320.55	44.60
33	1.005322	0.994734	329.06	44.54
34	1.005657	0.994403	337.44	44.48
35	1.006000	0.994063	345.71	44.42
36	1.006352	0.993716	353.85	44.37
37	1.006713	0.993360	361.89	44.33
38	1.007081	0.992997	369.81	44.29
39	1.007457	0.992626	377.64	44.25
40	1.007842	0.992247	385.36	44.22
41	1.008234	0.991861	392.99	44.20
42	1.008634	0.991467	400.52	44.18
43	1.009042	0.991067	407.97	44.16
44	1.009458	0.990659	415.33	44.15
45	1.009881	0.990244	422.60	44.15
46	1.010311	0.989822	429.80	44.14
47	1.010749	0.989393	436.91	44.15
48	1.011194	0.988957	443.95	44.15
49	1.011647	0.988515	450.92	44.16
50	1.012107	0.988066	457.81	44.17
51	1.012574	0.987610	464.64	44.19
52	1.013048	0.987148	471.40	44.21
53	1.013529	0.986680	478.10	44.24
54	1.014017	0.986205	484.74	44.26
55	1.014512	0.985723	491.32	44.29
56	1.015014	0.985236	497.84	44.33
57	1.015522	0.984743	504.30	44.37
58	1.016038	0.984243	510.71	44.41
59	1.016560	0.983737	517.07	44.45
60	1.017089	0.983226	523.38	44.50
61	1.017625	0.982708	529.64	44.55
62	1.018167	0.982185	535.85	44.61
63	1.018716	0.981655	542.02	44.66
64	1.019271	0.981120	548.14	44.72
65	1.019833	0.980580	554.22	44.79
66	1.020402	0.980034	560.26	44.85
67	1.020977	0.979482	566.26	44.92
68	1.021558	0.978924	572.22	45.00
69	1.022146	0.978361	578.15	45.07
70	1.022740	0.977793	584.04	45.15
71	1.023340	0.977219	589.89	45.23
72	1.023947	0.976640	595.72	45.32
73	1.024560	0.976056	601.51	45.40
74	1.025180	0.975466	607.27	45.49
75	1.025805	0.974871	613.00	45.59
76	1.026437	0.974271	618.71	45.68
77	1.027076	0.973665	624.39	45.78
78	1.027720	0.973055	630.04	45.88
79	1.028371	0.972439	635.67	45.99
80	1.029027	0.971819	641.27	46.10
81	1.029690	0.971193	646.86	46.21
82	1.030360	0.970562	652.42	46.32
83	1.031035	0.969926	657.96	46.44
84	1.031716	0.969286	663.48	46.56
85	1.032404	0.968640	668.98	46.68
86	1.033098	0.967990	674.47	46.81
87	1.033797	0.967335	679.94	46.94
88	1.034503	0.966674	685.40	47.07
89	1.035216	0.966009	690.84	47.20
90	1.035934	0.965340	696.26	47.34
91	1.036658	0.964665	701.68	47.48
92	1.037389	0.963986	707.08	47.63
93	1.038125	0.963302	712.48	47.77
94	1.038868	0.962613	717.86	47.93
95	1.039617	0.961920	723.24	48.08
96	1.040372	0.961222	728.60	48.24
97	1.041133	0.960519	733.96	48.40
98	1.041900	0.959812	739.32	48.56
99	1.042673	0.959100	744.67	48.73
100	1.043453	0.958384	750.01	48.90
101	1.044239	0.957662	755.36	49.07
102	1.045030	0.956937	760.70	49.25
103	1.045828	0.956207	766.03	49.43
104	1.046633	0.955472	771.37	49.62
105	1.047443	0.954733	776.71	49.80
106	1.048260	0.953989	782.05	50.00
107	1.049083	0.953240	787.39	50.19
108	1.049912	0.952488	792.73	50.39
109	1.050747	0.951730	798.07	50.59
110	1.051589	0.950968	803.42	50.80

Table 1-05



Specific Gravity and Temperature of Maximum Density of Seawater.

Table 1-06

Specific Volume of Distilled Water, in cm^3/g

	T, °C				
P, bars[a]	0	10	20	30	40
1	1.0000	1.0003	1.0017	1.0043	1.0078
100	0.9950	0.9956	0.9972	0.9999	1.0035

Table 1-06 Continued.

Specific Volume of Seawater

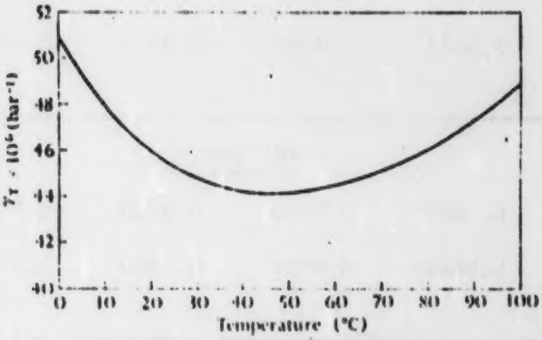
P, bars[a]	T, °C 0	10	20	30	40
			10 ^{0}/00 S		
1	0.9921	0.9926	0.9942	0.9968	1.0004
100	0.9873	0.9881	0.9899	0.9926	0.9961
			20 ^{0}/00 S		
1	0.9842	0.9850	0.9868	0.9894	0.9930
100	0.9796	0.9806	0.9826	0.9853	0.9888
			30 ^{0}/00 S		
1	0.9764	0.9775	0.9794	0.9821	0.9856
100	0.9719	0.9732	0.9753	0.9781	0.9816
			35 ^{0}/00 S		
1	0.9726	0.9738	0.9757	0.9784	0.9819
100	0.9681	0.9695	0.9717	0.9745	0.9780
			40 ^{0}/00 S		
1	0.9687	0.9700	0.9720	0.9748	0.9783
100	0.9644	0.9659	0.9680	0.9709	0.9744

Compressibility

The compressibility of water is relatively low (of the order of fifty parts per million per atmosphere at ordinary temperatures). Furthermore, it varies only relatively little with temperature. On a global scale, however, one could hardly afford to ignore the compressibility of water - especially if one lives in southern Florida - since were water completely incompressible, the level of the sea would be higher by about 40 meters (reducing the global land area by 5%).

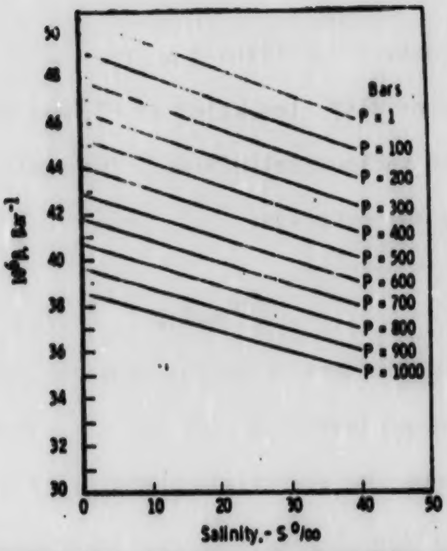
For extensive discussion of the compressibility of water, see Gmelin (loco cit., page 1331-1339).

For more recent studies of the isothermal compressibility of water, see the data by Millero, Curry and Drost-Hansen (1969).

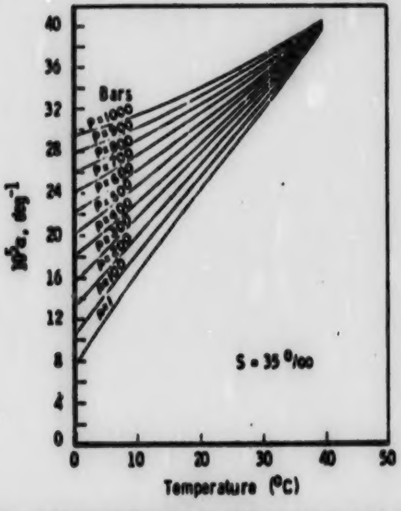


The coefficient of isothermal compressibility, γ_T, for liquid water at 1 atm pressure. Data from Kell (1967).

Figure 1-03



The Compressibility of Seawater at 0°C. From Wilson and Bradley (1966).



Coefficient of Thermal Expansion of Seawater as a Function of Temperature and Pressure. From Wilson and Bradley (1966).

Figure I-04

Specific gravity is defined as the ratio of density of solution to the density of distilled water at 4°, expressed as a function of temperature for various salinities. The results are given in terms of σ, defined by the equation:

$$\sigma_{s,T,p} = (\rho_{s,T,p} - 1)1000$$

where $\rho_{s,T,p}$ is the density of the seawater, depending on salinity, temperature and pressure. At (or near) 1 atmosphere pressure, it is customary to drop the subscripts s and p; as an example, $\sigma_T = 25.50$ implies a density of 1.02550. Figure 1-05 is taken from the illustration in the treatise edited by Kinne (1970, based on data by Knudsen, 1901).

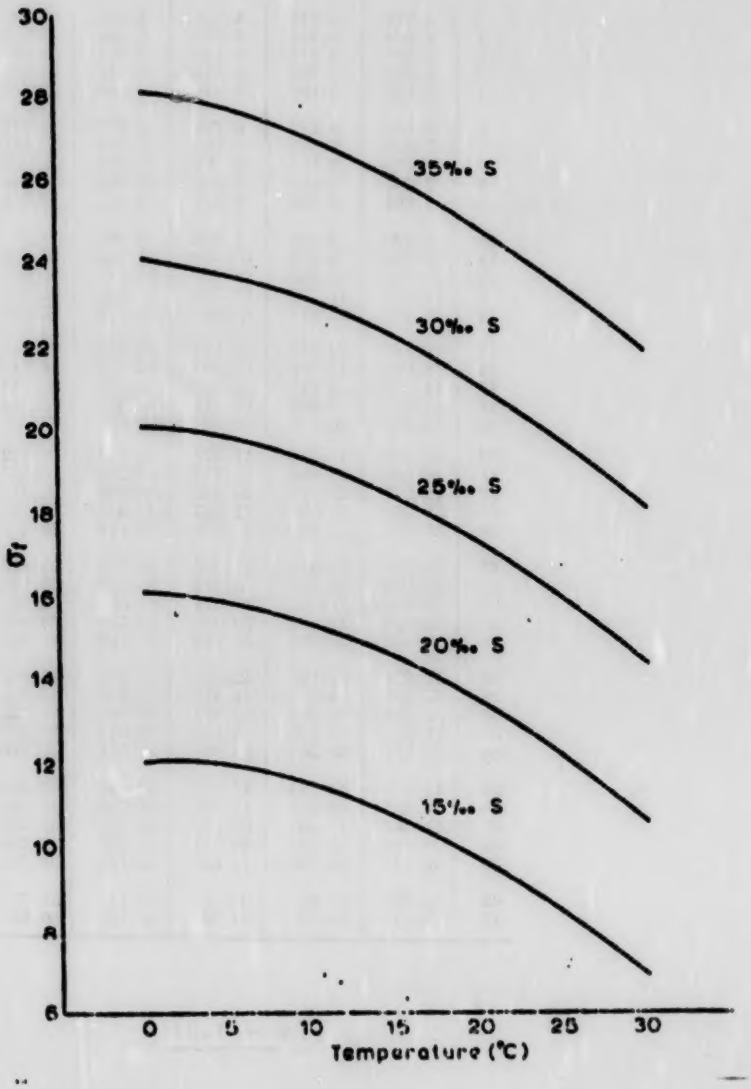

30
28
26
24
22
20
18
16
14
12
10
8
6
σ_t
0
5
10
15
20
25
30
Temperature (°C)
35‰ S
30‰ S
25‰ S
20‰ S
15‰ S

Figure 1-05

C. Vapor Pressure

VAPOR PRESSURE OF WATER BELOW 100°C

Pressure of aqueous vapor over water in mm of Hg for temperatures from −15.8 to 100°C. Values for fractional degrees between 50 and 89 were obtained by interpolation.

Temp. °C	0.0	0.2	0.4	0.6	0.8
−15	1.436	1.414	1.390	1.368	1.345
−14	1.560	1.534	1.511	1.485	1.460
−13	1.691	1.665	1.637	1.611	1.585
−12	1.834	1.804	1.776	1.748	1.720
−11	1.987	1.955	1.924	1.893	1.863
−10	2.149	2.116	2.084	2.050	2.018
− 9	2.326	2.289	2.254	2.219	2.184
− 8	2.514	2.475	2.437	2.399	2.362
− 7	2.715	2.674	2.633	2.593	2.553
− 6	2.931	2.887	2.843	2.800	2.757
− 5	3.163	3.115	3.069	3.022	2.976
− 4	3.410	3.359	3.309	3.259	3.211
− 3	3.673	3.620	3.567	3.514	3.461
− 2	3.956	3.898	3.841	3.785	3.730
− 1	4.258	4.196	4.135	4.075	4.016
− 0	4.579	4.513	4.448	4.385	4.320
0	4.579	4.647	4.715	4.785	4.855
1	4.926	4.998	5.070	5.144	5.219
2	5.294	5.370	5.447	5.525	5.605
3	5.685	5.766	5.848	5.931	6.015
4	6.101	6.187	6.274	6.363	6.453
5	6.543	6.635	6.728	6.822	6.917
6	7.013	7.111	7.209	7.309	7.411
7	7.513	7.617	7.722	7.828	7.936
8	8.045	8.155	8.267	8.380	8.494
9	8.609	8.727	8.845	8.965	9.086
10	9.209	9.333	9.458	9.585	9.714
11	9.844	9.976	10.109	10.244	10.380
12	10.518	10.658	10.799	10.941	11.085
13	11.231	11.379	11.528	11.680	11.833
14	11.987	12.144	12.302	12.462	12.624
15	12.788	12.953	13.121	13.290	13.461
16	13.634	13.809	13.987	14.166	14.347
17	14.530	14.715	14.903	15.092	15.284
18	15.477	15.673	15.871	16.071	16.272
19	16.477	16.685	16.894	17.105	17.319
20	17.535	17.753	17.974	18.197	18.422
21	18.650	18.880	19.113	19.349	19.587
22	19.827	20.070	20.316	20.565	20.815
23	21.068	21.324	21.583	21.845	22.110
24	22.377	22.648	22.922	23.198	23.476
25	23.756	24.039	24.326	24.617	24.912
26	25.209	25.509	25.812	26.117	26.426
27	26.739	27.055	27.374	27.696	28.021
28	28.349	28.680	29.015	29.354	29.697
29	30.043	30.392	30.745	31.102	31.461
30	31.824	32.191	32.561	32.934	33.312
31	33.695	34.082	34.471	34.864	35.261
32	35.663	36.068	36.477	36.891	37.308
33	37.729	38.155	38.584	39.018	39.457
34	39.898	40.344	40.796	41.251	41.710
35	42.175	42.644	43.117	43.595	44.078
36	44.563	45.054	45.549	46.050	46.556
37	47.067	47.582	48.102	48.627	49.157
38	49.692	50.231	50.774	51.323	51.879
39	52.442	53.009	53.580	54.156	54.737
40	55.324	55.91	56.51	57.11	57.72
41	58.34	58.96	59.58	60.22	60.86

Table I-07

D. Heat of Vaporization

The heat of vaporization of water has been discussed by Dorsey (1940) and Gmelin (loco cit., page 1363-1367). Table 1-08 gives the values for the heat of vaporization (in international calories/gram from Gmelin (page 1364).

Table 1-08

Temperature	ΔH_{l-g}
0°	597.3
10°	591.7
20°	586.0
30°	580.4
40°	574.7
50°	569.0
60°	563.2
70°	557.3
80°	551.3
90°	545.2
100°	539.0

E. Specific Heat

The physico-chemical properties of water which are most important in determining global ecology are vapor pressure, heat of vaporization and specific heat. Vapor pressure data are shown in the overview of physical properties of water, Table I-01. The heat of vaporization is discussed very briefly in Section D. Detailed Tables of the specific heat are given below. Franks (1968) has reminded us of the enormous influence of the large heat capacity of water in affecting our terrestrial environment. Franks observes: "If we consider a warm ocean current such as the Gulfstream, 100 miles wide and a quarter mile deep, flowing at one mile/h from a warm to a cold region, with a temperature gradient of 20° C, then the thermal energy transport every hour is equivalent to that supplied by 1.75×10^8 tons of coal. All the coal mined in the world in one year is able to supply heat at this rate for only one and a half hours."

The specific heat of the water has been discussed in detail by Dorsey (1940) and in Gmelin (loco cit., page 1370-1375).

Figure I-06 shows the overall behavior of c_p, and c_v between 0 and 100° C (from Eisenberg **and Kauzmann**, 1969). A more detailed graph is shown in Figure I-07 (data by Ginnings and Furukawa, 1953; see Kinne, 1970 (Vol. I, Pt. I, Chapter 3.0 - p. 323). It is seen that the specific heat at constant pressure goes through a shallow maximum in the vicinity of 35° C.

A Table of recommended values (Table I-08) is taken from Gmelin (pp. 1372-1373). (c_p is expressed in absolute joules/gram/degree).

Figure 1-06

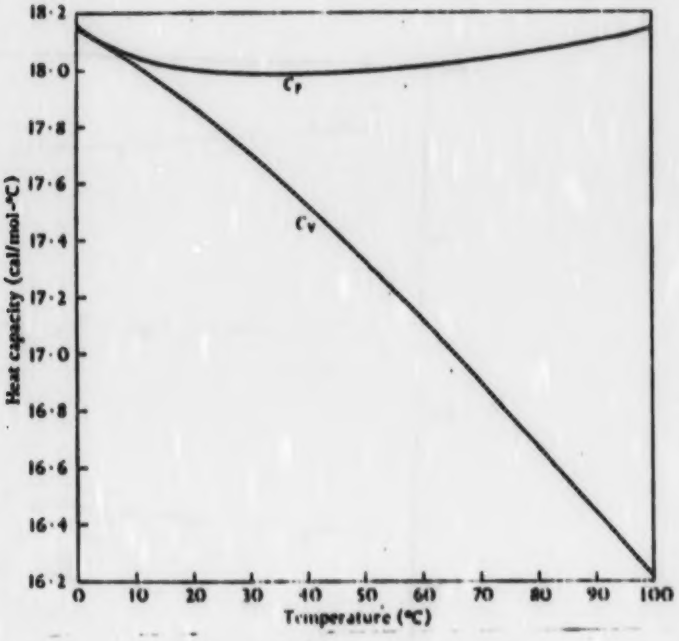
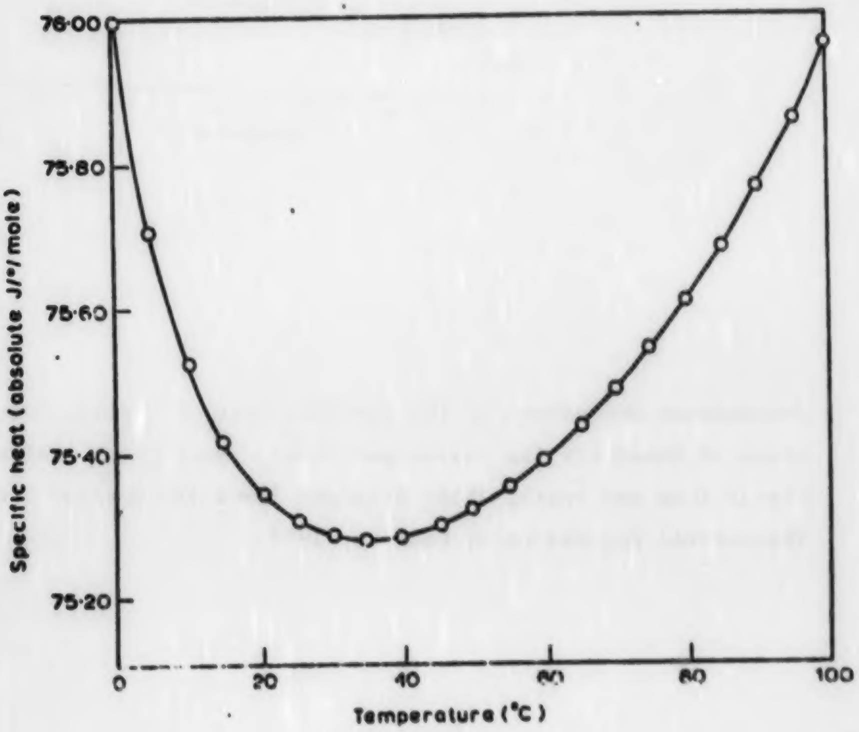
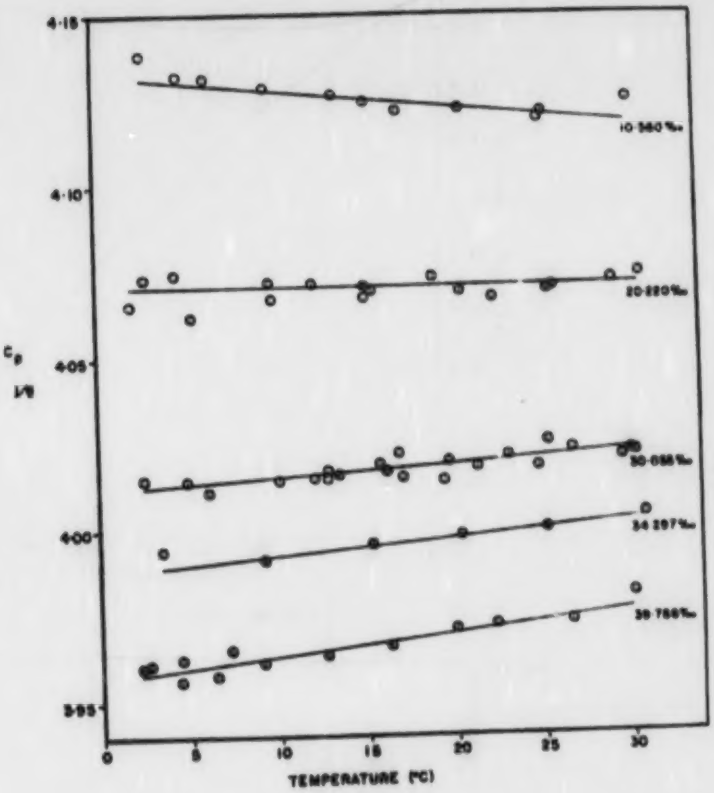


Figure 1-07





Temperature Dependence of the Specific Heat of Various Concentrations of Seawaters (in Joules per Gram). Data point indicated by Circle (Cox and Smith, 1959; Straight lines are Derived from Theoretical Expression by Conners, 1970).

Figure I-08

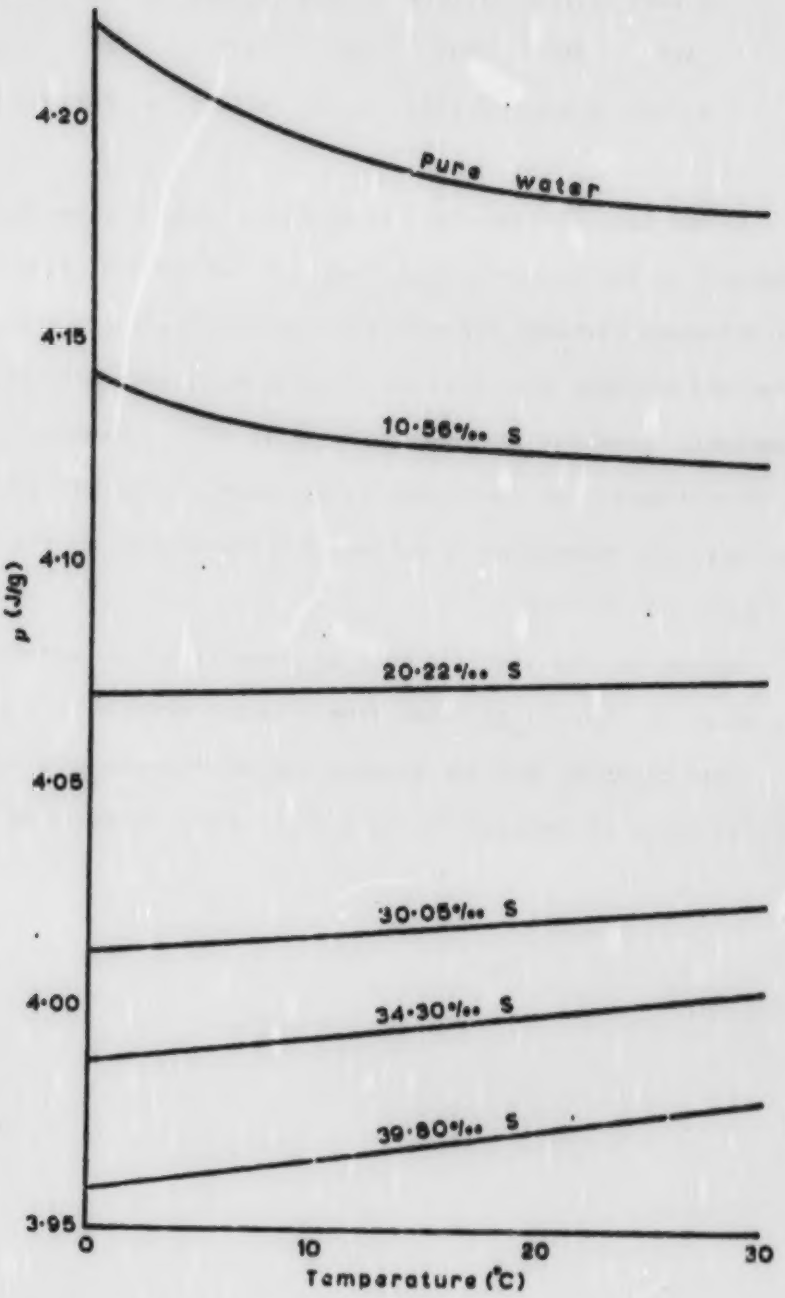

4·20
4·15
4·10
4·05
4·00
3·95
p (J/g)
Pure water
10·56‰ S
20·22‰ S
30·05‰ S
34·30‰ S
39·80‰ S
0
10
20
30
Temperature (°C)

Figure 1-09

Table 1-08

t	0°	2°	4°	6°	8°	10°	12°	14°	15°
c_p	4.2177	4.2107	4.2048	4.1999	4.1957	4.1922	4.1893	4.1869	4.1858
t	16°	18°	20°	22°	24°	26°	28°	30°	32°
c_p	4.1849	4.1832	4.1819	4.1808	4.1800	4.1793	4.1788	4.1785	4.1783
t	34°	36°	38°	40°	42°	44°	46°	48°	50°
c_p	4.1782	4.1783	4.1784	4.1786	4.1789	4.1792	4.1797	4.1802	4.1807

It has been claimed that the specific heat of water is relatively dependent on the amount of dissolved air (see Gmelin, loco cit., page 1374). The difference between the apparent specific heats of carefully degassed water and ordinary distilled water (presumably saturated with air) is remarkably large (of the order of 0.5% at 40°). However, there appears to be no theoretical justification for such a large difference· on the contrary, the theoretically estimated difference is of the order of only six parts per million.

Values for the specific heat of seawater of variant composition are shown in Figure 1-08 taken from a recent article by Conners (1970).

Heat capacity data for aqueous sodium chloride solutions over a partial range of interest in the present study is shown in Table 1-09.

Heat capacity data for aqueous sodium chloride solutions are shown for four different temperatures over a wide concentration range in Table I-09 (Parker, 1965). The concentrations are expressed in molal concentrations (m; the variable n is the ratio of water molecules to "molecules" of sodium chloride).

Table I-09

Φ_c, cal/deg mole

n	m	15°	20°	25°	30°
∞	0.00	−25.2	−23.3	−21.5	−20.1
100,000	.000555	−25.1	−23.2	−21.4	−20.0
50,000	.00111	−25.0	−23.1	−21.3	−19.9
20,000	.00278	−24.9	−23.0	−21.2	−19.8
10,000	.00555	−24.8	−22.9	−21.1	−19.6
7,000	.00793	−24.7	−22.8	−21.0	−19.5
5,000	.01110	−24.6	−22.7	−20.9	−19.4
4,000	.01388	−24.5	−22.6	−20.8	−19.3
3,000	.01850	−24.4	−22.5	−20.7	−19.2
2,000	.02775	−24.2	−22.3	−20.4	−19.0
1,500	.03700	−23.9	−22.0	−20.2	−18.8
1,000	.05551	−23.4	−21.6	−19.8	−18.4
900	.0617	−23.3	−21.4	−19.6	−18.2
800	.0694	−23.1	−21.3	−19.5	−18.1
700	.0793	−22.8	−21.0	−19.3	−17.9
600	.0925	−22.5	−20.8	−19.0	−17.6
500	.1110	−22.0	−20.3	−18.6	−17.3
400	.1388	−21.4	−19.8	−18.2	−16.9
300	.1850	−20.5	−19.0	−17.5	−16.2
200	.2775	−19.0	−17.5	−16.3	−15.1
150	.3700	−17.7	−16.4	−15.2	−14.1
100	.5551	−15.5	−14.8	−13.4	−12.5
75	.7401	−13.6	−12.6	−11.7	−10.9
50	1.1101	−10.4	−9.6	−8.8	−8.2
40	1.3877	−8.3	−7.6	−7.0	−6.4
30	1.8502	−5.7	−5.1	−4.6	−4.1
25	2.2202	−3.5	−2.9	−2.4	−2.0
20	2.7753	−0.8	−0.4	0.0	+0.2
15	3.7004	....	....	+3.3	3.5
12	4.6255	....	....	6.3	....
10	5.5506	....	....	9.0	....
9.5	5.8427	....	....	9.7	....
9.0	6.1674	....	....	10.5	....

F. Thermal Conductivity

For a discussion of the heat conductivity of water (and ice), see Dorsey (1940) and particularly Gmelin (loco cit., p. 1403-1408). In passing, it is noted that the heat conductivity of ice is notably larger- as would be expected theoretically - than that of liquid water. Values for the heat conductivity of ice single crystals appears to depend on the orientation (parallel to or perpendicular to the C-axis - a difference of about 5%). Values reported in the literature for ice at -4° range from 0.016 to 0.020 w/cm/°. Values for the heat conductivity of liquid water are shown in the Table below.

Table I-10

Temp.	0°	10°	20°	30°	40°	50°	60°	70°	80°
$10^5 k''$	560	581	600	$614._5$	$628._5$	641	653	662	$669._5$

(all values in watts/centimeter/degree. Note conversion factor 1 watt/cm/° = 0.23899 cal/cm/sec/°.)

G. Viscosity

Recent data for the viscosity of pure water as a function of temperature are shown in Table I-11, which gives the viscosity (in centipoises) by five different sets of co-workers. Within the limits of primary interest, the data generally seem to be in good agreement nutually.

Pressure exerts a notable effect on the viscosity of water. Some viscosity isotherms are shown in Figure I-10.

Finally, Figure I-11 shows a comparison between the viscosity and the thermal conductivity for water (and heavy water) over a wide temperature range.

Some older data for the viscosity of seawater (reported in millipoise) are reported in Table I-12 (data by Miyake and Koizumi, 1948).

More recent data are shown in survey form for an extended temperature range for salinities varying from 10.0 grams/kilogram to 150 grams/kilogram (and up to high temperatures). (Data by Isdale, Spence and Tudhope, 1972). (See Table I-13).

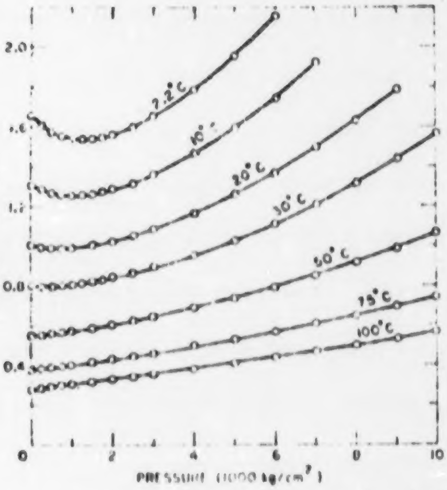
Other recent viscosity measurements of seawater have been made by various authors. Figure I-12 shows the results reported by Horne et al (1965). Other data have been reported by Fabuss and Korosi (1967, 1969a). See also Emerson and Jamieson (1967). Recent data of high precision have also been obtained in the present author's laboratory by Dexter (1970). Low temperature data have been reported by Eicher and Zwolinski (1971).

Table 1-11

Viscosity of H_2O at Atmospheric Pressure[a]

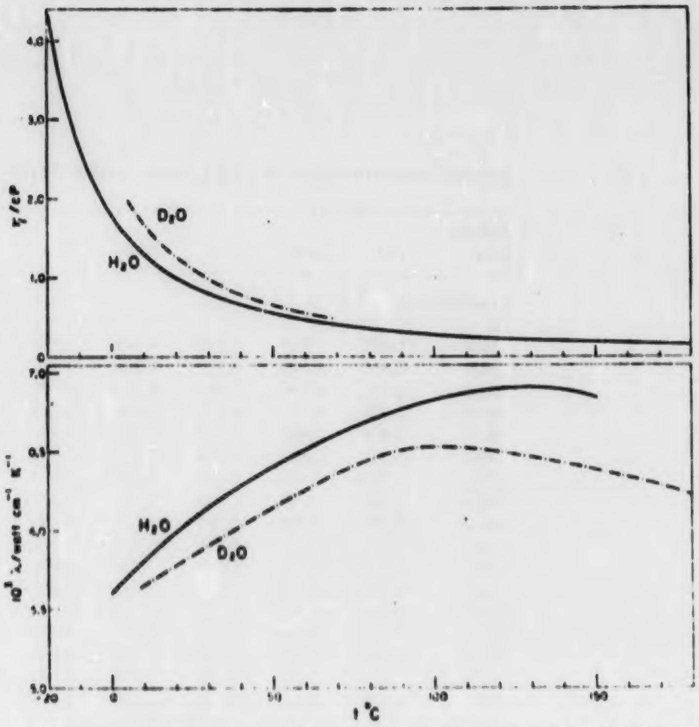
t_{90}, °C	Viscosity, cP				
	Stokes and Mills[illegible]	Korosi and Fabuss[illegible]	Korson *et al.*[illegible]	Weber[illegible]	Hardy and Cottington[illegible]
0	1.787	—	1.7916	1.792	—
5	1.516	—	1.5192	1.520	1.5184
10	1.306	—	1.3069	1.3069	—
15	1.138	—	1.1382	1.1383	—
20	1.002	1.0020	1.0020	1.0020	—
25	0.8903	0.8903	0.8903	0.8903	—
30	0.7975	—	0.7975	0.7975	—
35	0.7194	—	0.7195	0.7193	—
40	0.6531	0.6527	0.6532	0.6531	0.6531
45	0.5963	—	0.5963	—	—
50	0.5467	—	0.5471	—	—
55	0.5044	—	0.5042	—	—
60	0.4666	0.4665	0.4666	—	0.4665
65	0.4342	—	0.4334	—	—
70	0.4049	0.4045	0.4039	—	—
75	0.3788	0.3784	0.3775	—	—
80	0.3554	0.3546	0.3538	—	0.3548
85	0.3345	—	0.3323	—	—
90	0.3156	0.3143	0.3128	—	0.3148
95	0.2985	—	0.2949	—	0.2976
100	0.2829	0.2820	0.2783	—	0.2822

[a] All values here are adjusted to a value of 1.002 cP at 20°C.



Viscosity of water under pressure. The data shown indicate that $(\partial\eta/\partial P)_T = 0$ at 33.5 C. Reproduced from Bett and Cappi.[illegible] (Reprinted with permission from *Nature*, copyright 1965.)

Figure 1-10



Transport properties of liquid at atmospheric pressure. (a) Viscosity η. (b) Thermal conductivity λ. For D_2O, the values up to 60°C are the means given by Powell,[(8)] and those above 75 C are from Ziebland and Burton.[(1160)]

Figure 1-11

Table 1-12

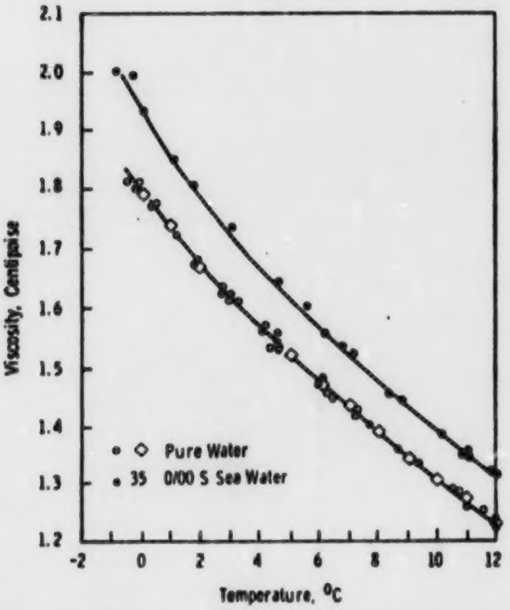
Viscosity coefficients of sea water in millipoise
(After Miyake and Koizumi, 1948)

°C	Cl °/₀₀ 0	4	8	12	16	20
0	17·94	18·11	18·29	18·45	18·62	18·90
2	16·76	16·92	17·10	17·29	17·46	17·74
4	15·73	15·65	16·03	16·25	16·41	16·68
6	14·75	14·89	15·07	15·28	15·46	15·71
8	13·81	14·03	14·20	14·41	14·59	14·83
10	13·10	13·24	13·41	13·62	13·80	14·03
12	12·30	12·52	12·69	12·89	13·07	13·29
14	11·73	11·87	12·04	12·23	12·40	12·60
16	11·13	11·27	11·43	11·61	11·79	11·97
18	10·58	10·72	10·88	11·05	11·21	11·39
20	10·07	10·21	10·36	10·52	10·68	10·85
22	9·60	9·74	9·89	10·03	10·19	10·35
24	9·16	9·30	9·45	9·58	9·73	9·88
26	8·75	8·90	9·04	9·16	9·31	9·41
28	8·37	8·52	8·65	8·77	8·91	9·04
30	8·02	8·17	8·30	8·40	8·54	8·66

DYNAMIC VISCOSITY OF SEA WATER SOLUTIONS, mNs m^{-2} (cP)

Salinity g/kg	*10.0*	*30.0*	*35.0*	*50.0*	*70.0*	*90.0*	*110.0*	*130.0*	*150.0*
Temperature °C									
20.0	1.019	1.059	1.070	1.105	1.158	1.218	1.284	1.357	1.437
30.0	0.812	0.846	0.855	0.884	0.928	0.976	1.029	1.087	1.150
40.0	0.666	0.694	0.702	0.727	0.764	0.804	0.848	0.896	0.947
50.0	0.558	0.583	0.590	0.611	0.643	0.677	0.714	0.754	0.797
60.0	0.476	0.498	0.504	0.523	0.551	0.581	0.613	0.647	0.684
70.0	0.413	0.433	0.438	0.455	0.479	0.505	0.534	0.564	0.595
80.0	0.363	0.381	0.385	0.400	0.422	0.446	0.471	0.497	0.525
90.0	0.322	0.339	0.343	0.356	0.376	0.397	0.420	0.444	0.469
100.0	0.289	0.304	0.308	0.320	0.338	0.357	0.378	0.399	0.422
110.0	0.261	0.275	0.279	0.290	0.306	0.324	0.343	0.363	0.383
120.0	0.238	0.251	0.254	0.264	0.280	0.296	0.313	0.331	0.351
130.0	0.218	0.230	0.233	0.243	0.257	0.272	0.288	0.305	0.323
140.0	0.201	0.212	0.215	0.224	0.237	0.251	0.266	0.282	0.298
150.0	0.186	0.196	0.199	0.207	0.220	0.233	0.247	0.262	0.277
160.0	0.173	0.183	0.185	0.193	0.205	0.217	0.230	0.244	0.259
170.0	0.161	0.170	0.173	0.180	0.191	0.203	0.215	0.229	0.243
180.0	0.151	0.160	0.162	0.169	0.179	0.190	0.202	0.215	0.228

Table 1-13



Temperature Dependence of the Viscosities of Pure Water (open circles) and 35‰ *S* Seawater (closed circles). From Horne, Courant, Johnson, and Margosian (1965), with permission of American Chemical Society.

Figure 1-12

H. Diffusion Coefficient

For a discussion of the self-diffusion coefficient of water (i.e., water in water) determined by the use of various tracers (such as D_2O, DHO, HTO, H_2O^{18} and $D_2{}^{18}O$) see Gmelin (loco cit., page 1472). Characteristic values from Gmelin are shown in Table 1-14.

Table 1-14

t	0°	5°	15°	25°	35°	45°	55°
$D \cdot 10^5$	1.00	1.20	1.61	2.13	2.76	3.45	4.16
$D \cdot 10^5$	----	----	1.62 ±0.03	2.04	2.73 ±0.04	3.34 ±0.08	----

as reported by two different investigators.

The effect of electrolytes on the self-diffusion of water has been studied by Devell (1962), and a thorough discussion of diffusion in water in aqueous solutions in general, has been presented by McCall and Douglass (1965).

Table 1-15 lists some values for the diffusion coefficients of some electrolytes in water at 25°, as a function of concentration.

Table 1-15

Diffusion Coefficients of Some Seawater Electrolytes at 25°C

Concentration, *M*	NaCl	KCl	CsCl	$CaCl_2$	$SrCl_2$	Na_2SO_4	$MgSO_4$
				$cm^2/sec \times 10^5$			
0.005	1.560	1.934	1.978	1.179	1.219	1.123	0.710
0.01	1.545	1.917	1.958	—	—	—	—
0.05	1.507	1.864	—	—	—	—	—
0.10	1.483	1.844	1.971	—	—	—	—
0.50	1.474	1.850	1.860	—	—	—	—
1.00	1.404	1.892	1.902	—	—	—	—
1.50	1.473	1.943	—	—	—	—	—

1. Surface Tension

The surface tension of water has been determined repeatedly. The values recommended in Gmelin (loco cit., page 1420) are shown in Table 1-16 below.

Table 1-16

Temp.	0	1	2	3	4	5	6	7	8	9
0°	75.626	75.470	75.312	75.155	75.006	74.860	74.713	74.555	74.410	74.263
10°	74.113	73.957	73.800	73.653	73.497	73.350	73.203	73.045	72.889	72.732
20°	72.583	72.427	72.270	72.113	71.957	71.810	71.652	71.495	71.339	71.192
30°	71.035	70.869	70.710	70.539	70.397	70.230	70.073	69.906	69.740	69.573
40°	69.416	69.249	69.083	68.925	68.739	68.592	68.424	68.257	68.091	67.914
50°	67.799	67.571	67.405	67.238	67.072	66.894	66.717	66.341	66.374	66.208

Note, however, that more recent determinations with likely greater accuracy and precision have been reported by a number of authors (Gitten, 1969); Johansson and Eriksson (1972); and Cini and co-workers (1972).

Surface tension values for seawater have been reported infrequently: the reason for the lack of data is the frequent incident of naturally-occurring surface-active agents tending to yield significantly lower values than theoretically predicted (and often with considerable scatter). A table of "Surface Tension of Clean Seawater" presented in the Table below.

Table 1-17

Surface Tension of Clean Seawater
(From Fleming and Revelle, 1939, with permission of American Association of Petroleum Geologists)

	Temperature, °C			
S, ‰	0	10	20	30
0	75.64	74.20	72.76	71.32
10	75.86	74.42	72.98	71.54
20	76.08	74.64	73.20	71.76
30	76.30	74.86	73.42	71.98
35	76.41	74.97	73.53	72.09
40	76.52	75.08	73.64	72.20

J. Dielectric Constant

The static dielectric constant of water decreases with temperature. For a review of measurements of this quantity, see Gmelin (loco cit., page 1591-1592). The dielectric constant of water is obviously one of the most important parameters in connection with the suitability of water to support life, through its role in determining the solubility and dissociation of electrolytes. Figure 1-13 shows the dielectric constant of water as a function of temperature, taken from the review of seawater in the treatise by Kinne (1963), based on data by Weast.

Table 1-18 shows the microwave dielectric data and relaxation parameters for water as a function of temperature. These measurements were reported by Hasted and co-workers (see Franks, 1972, page 277). In this Table is given the static dielectric constant (ε_s), the high-frequency dielectric constant (ε_∞), the relaxation time (τ) x 10^{-11} seconds.

Table 1-18

Microwave Dielectric Data and Relaxation Times

T,°C	ε_s	ε_∞	τ,X10^{-11} sec
0	88.3	4.46	1.79
10	84.1	4.10	1.26
20	80.4	4.23	0.93
30	76.8	4.20	0.72
40	73.2	4.16	0.58
50	70.0	4.13	0.48
60	66.6	4.21	0.39
75	62.1	4.49	0.32

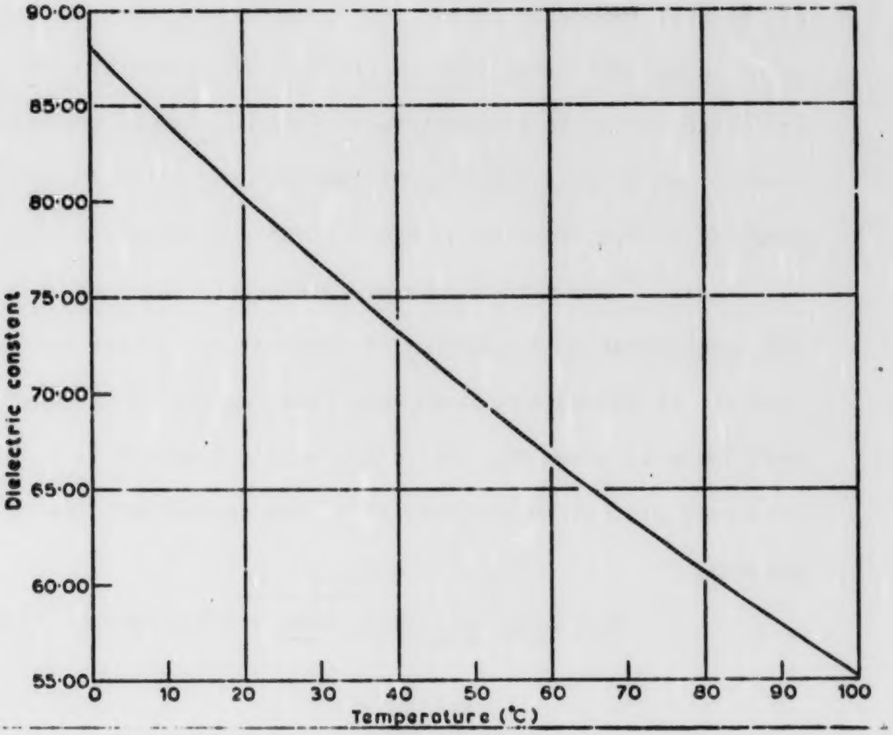

90·00
85·00
80·00
75·00
70·00
65·00
60·00
55·00
Dielectric constant
0
10
20
30
40
50
60
70
80
90
100
Temperature (°C)

Figure 1-13

K. Index of Refraction.

Table I-19

Refractive Index of Seawater[a]

(From C. L. Utterback, T. G. Thompson, and B. D. Thomas, *J. Conseil Exploration Mer*, 9, 35 (1934) with permission of Conseil International pour l'Exploration.)

	Temperature, °C					
S, ‰	0	5	10	15	20	25
0	1.3 3395	1.3 3385	1.3 3370	1.3 3340	1.3 3300	1.3 3250
5	3500	3485	3465	3435	3395	3345
10	3600	3585	3565	3530	3485	3435
15	3700	3685	3660	3625	3580	3525
20	3795	3780	3750	3715	3670	3620
25	3895	3875	3845	3805	3760	3710
30	3991	3966	3935	3898	3851	3798
31	4011	3985	3954	3916	3869	3816
32	4030	4004	3973	3934	3886	3834
33	4049	4023	3992	3953	3904	3851
34	4068	4042	4011	3971	3922	3868
35	4088	4061	4030	3990	3940	3886
36	4107	4080	4049	4008	3958	3904
37	4127	4099	4068	4026	3976	3922
38	4146	4118	4086	4044	3994	3940
39	4166	4139	4105	4062	4012	3958
40	(4185)	(4157)	(4124)	(4080)	(4031)	(3976)
41	(4204)	(4716)	(4143)	(4098)	(4049)	(3994)

[a] For sodium D light.

The value for the Index of Refraction of seawater as a function of both temperature and salinity. Reported by Horne (1969), p. 517).

L. Electrical Conductivity

The electrical conductivity of pure water has been reported by various authors. For a summary, see, for instance, Gmelin (1963). Because the electrical conductivity of water is extremely sensitive to electrolytic impurities and particularly to the presence of dissolved CO_2, data for the conductivity of pure water are not listed here.

A large literature exists on the problem of the electrical conductivity of seawater. For specific applications, the reader is referred to the oceanographic literature for details. A survey taken of the specific conductivity of water as a function of temperature and salinity is shown in Table 1-20. See also Figure 1-14.

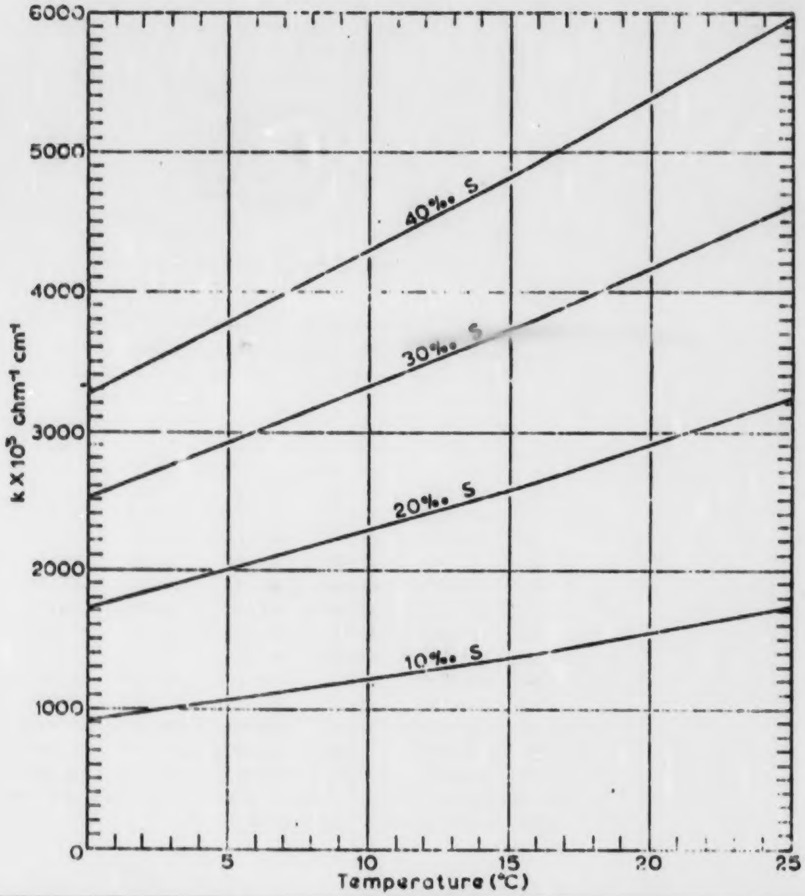
Table 1-20

Specific Conductivity of Seawater[a]

[Values calculated from the equation of P. Weyl, *Limnol. Oceanog.*, 9, 75 (1964), based on data of B. D. Thomas, T. G. Thompson, and C. L. Utterback, *J. Conseil Perm. Intern. Exploration Mer.*, 9, 28 (1934)]

	Temperature, °C						
S, ‰	30	25	20	15	10	5	0
10	(19.127)	17.345	15.628	13.967	12.361	10.816	9.341
20	(35.458)	32.188	29.027	25.967	23.010	20.166	17.456
30	(50.856)	46.213	41.713	37.351	33.137	29.090	25.238
31	(52.360)	47.584	42.954	38.467	34.131	29.968	26.005
32	(53.859)	48.951	44.192	39.579	35.122	30.843	26.771
33	(55.352)	50.314	45.426	40.688	36.110	31.716	27.535
34	(56.840)	51.671	46.656	41.794	37.096	32.588	28.298
35	(58.323)	53.025	47.882	42.896	38.080	33.457	29.060
36	(59.801)	54.374	(49.105)	(43.996)	(39.061)	(34.325)	(29.820)
37	(61.274)	55.719	(50.325)	(45.093)	(40.039)	(35.190)	(30.579)
38	(62.743)	57.061	(51.541)	(46.187)	(41.016)	(36.055)	(31.337)
39	(64.207)	58.398	(52.754)	(47.278)	(41.990)	(36.917)	(32.094)
40	(65.667)	(59.732)	(53.963)	(48.367)	(42.962)	(37.778)	(32.851)

[a] Conductivity in $\text{ohm}^{-1}\,\text{cm}^{-1} \times 1000$.



6000
5000
4000
3000
2000
1000
0
k X 10³ ohm⁻¹ cm⁻¹
40‰ S
30‰ S
20‰ S
10‰ S
5
10
15
20
25
Temperature (°C)

Figure 1-14

Table 1-21 shows the temperature dependencies of cation and anion equivalent conductances (at infinite dilution).

	0 °C	18 °C	25 °C	100 °C
$l'_{1\infty}$				
$H^{\cdot}$	224	315	349,8	631
$Li^{\cdot}$	19,3	32,6	38,7	116
$Na^{\cdot}$	25,7	42,6	50,1	148
$K^{\cdot}$	40,3	63,7	73,5	193
$Rb^{\cdot}$	43,5	66,3	77	—
$Cs^{\cdot}$	43	66,8	77,7	200
$Ag^{\cdot}$	33	53,3	62,2	180
$Tl^{\cdot}$	43,3	64,8	74	—
$NH_4^{\cdot}$	40,0	63,6	74	184
$N(CH_3)_4^{\cdot}$	23,0	39,7	41,5	—
$N(C_2H_5)_4^{\cdot}$	15,8	27,2	32	100
$^1/_2\,Be^{\cdot\cdot}$	—	—	45	—
$^1/_2\,Mg^{\cdot\cdot}$	31	44,6	58	170
$^1/_2\,Ca^{\cdot\cdot}$	30,5	50,4	59	187
$^1/_2\,Sr^{\cdot\cdot}$	30	50,6	60	—
$^1/_2\,Ba^{\cdot\cdot}$	32	54,4	63,2	200
$^1/_2\,Ra^{\cdot\cdot}$	(33)	56,5	(66,8)	—
$^1/_2\,Mn^{\cdot\cdot}$	23,5	44,5	50	—
$^1/_2\,Fe^{\cdot\cdot}$	28	(44,5)	(53,5)	—
$^1/_2\,Co^{\cdot\cdot}$	28	45	49	—
$^1/_2\,Ni^{\cdot\cdot}$	23	45	49	—
$^1/_2\,Cu^{\cdot\cdot}$	28	45,3	55,5	—
$^1/_2\,Zn^{\cdot\cdot}$	27,0	45	54	—
$^1/_2\,Cd^{\cdot\cdot}$	28	45,1	54	—
$^1/_2\,Pb^{\cdot\cdot}$	37,5	60	65	—
$^1/_3\,Al^{\cdot\cdot\cdot}$	29	—	61	—
$^1/_3\,Sc^{\cdot\cdot\cdot}$	—	—	64,7	—
$^1/_3\,Y^{\cdot\cdot\cdot}$	32	—	62	—
$^1/_3\,La^{\cdot\cdot\cdot}$	35	59,2	69,7	220
$^1/_3\,Ce^{\cdot\cdot\cdot}$	—	—	67	—
$^1/_3\,Pr^{\cdot\cdot\cdot}$	—	—	65,4	—
$^1/_3\,Nd^{\cdot\cdot\cdot}$	—	—	64,3	—
$^1/_3\,Sm^{\cdot\cdot\cdot}$	32	—	62	—
$^1/_3\,Gd^{\cdot\cdot\cdot}$	31,9	—	62	—
$^1/_3\,Co(NH_3)_6^{\cdot\cdot\cdot}$	56	—	100	—
$l'_{2\infty}$				
OH'	105	174	197	440
F'	—	47,6	55	—
Cl'	41,4	66,3	76,4	213
ClO_3'	36	55,8	65,3	172
ClO_4'	37,3	59,1	67	183
Br'	43,1	68,3	78	180
BrO_3'	30,7	49,0	56,0	155
J'	42,6	66,8	77,1	—
JO_3'	20,7	34,8	41,6	127
NO_3'	40,2	62,6	71,1	191
CN'	—	—	82	—
SCN'	37,0	57,4	66	—
MnO_4'	36	53	61	—
$HCOO'$	—	48	54	86
CH_3COO'	23,5	35	41,4	90
$^1/_2\,SO_4''$	40,7	68,7	79	230
$^1/_2\,S_2O_3''$		—	84,9	—
$^1/_2\,CO_3''$	36	60,5	74,0	—
$^1/_2\,CrO_4''$	44	72	83	—
$^1/_3\,Fe(CN)_6'''$	—	—	94	—
$^1/_4\,Fe(CN)_6''''$	57,5	—	100	278

PART I

SECTION III: SOLUTION PROPERTIES

III.A.1. Ion Activities

The effect of temperature on thermodynamic equilibrium properties is generally well understood, and readily described. For the systems of interest to natural waters all the necessary input data for a systematic description of the chemistry as a function of temperature, however, not necessarily available. Theoretical estimates are readily obtained by the use of the Debye-Hückel equation or one of its extensions. Yet, it is recognized that serious limitations are implied in either more concentrated solutions (say, for ionic strength of 0.5 or above) or in the presence of several types of ionic species, particularly those prone to form ion complexes. A good discussion of a chemical model for seawater is presented by Garrels and Thompson (1962); see also Garrels and Christ). Generally, for seawater, an ionic strength of 0.7 is accepted - a value certainly sufficiently accurate for the purposes of the present discussion. Note that an ionic strength of 0.7 is high enough to cause interactions between ions which change their thermodynamic properties so as to yield quantitative data notably different from those one would obtain by ignoring complex formation. The average composition of surface seawater (19 parts per thousand chlorinity) at 25° is given below (Garrels and Christ, p. 101): see Table I-22

Table I-23, taken from Garrels and Christ (p. 103) gives the activity coefficients of individual species at ionic strength of 0.7 (chlorinity 19 parts per thousand; 25°C).

Of interest in the present connection is the change of these activities - differing from those estimated on the simple use of a Debye-Hückel type of equation - due to temperature.
However, it is obvious that while no accurate estimates can be made through extensions of the Debye-Hückel equation, some generalities of

Table 1-22

Composition of Average Surface Sea Water with 19‰ (parts per thousand) Chlorinity at 25 °C (pH = 8.15)

Ion	Molality
Na^+	0.48
Mg^{++}	0.054
Ca^{++}	0.010
K^+	0.010
Cl^-	0.56
SO_4^{--}	0.028
HCO_3^-	0.0024
CO_3^{--}	0.00027

Table 1-23

Activity Coefficients of Individual Species in Sea Water.* (Ionic Strength, 0.7; Chlorinity, 19‰, 25 °C)

Dissolved Species	Activity Coefficient	Method Used
$NaHCO_3^0$	1.13	Analogy with H_2CO_3
$MgCO_3^0$	1.13	Same
$CaCO_3^0$	1.13	Same
$MgSO_4^0$	1.13	Same
$CaSO_4^0$	1.13	Same
HCO_3^-	0.68	Figure 4.5, A
$NaCO_3^-$	0.68	Analogy with HCO_3^-
$NaSO_4^-$	0.68	Same
KSO_4^-	0.68	Same
$MgHCO_3^+$	0.68	Same
$CaHCO_3^+$	0.68	Same
Na^+	0.76	Meas. glass electrode
K^+	0.64	$\gamma_{K^+} = \gamma_{\pm KCl}$
Mg^{++}	0.36	$\gamma_{Mg^{++}} = (\gamma^2_{\pm MgCl_2})/(\gamma^2_{\pm KCl})$
Ca^{++}	0.28	$\gamma_{Ca^{++}} = (\gamma^2_{\pm CaCl_2})/(\gamma^2_{\pm KCl})$
Cl^-	0.64	$\gamma_{Cl^-} = \gamma_{\pm KCl}$
CO_3^{--}	0.20	Figure 4.5, D
SO_4^{--}	0.12	See text

significance can still be derived. Thus, the temperature effects will be reflected, respectively, in the A and B coefficients, primarily. The temperature variations of these constants are shown in Table I-24 (taken from the extensive calculations by Hamer, 1968). It is obvious that no sudden or abrupt changes are to be expected over the temperature range of interest in connection with natural waters.

Table I-24

Values of the Debye-Hückel constants for activity coefficients based on the values of the dielectri constant of water determined by Owen et al. [12]

t °C	ϵ[a]	*A*		*B*	
		Weight basis	Volume basis	Weight basis	Volume basis
		$kg^{1/2}\ mol^{-1/2}$	$l^{1/2}\ mol^{-1/2}$	$kg^{1/2} 10^8\ cm\ mol^{-1/2}$	$l^{1/2} 10^8\ cm\ mol^{-1/2}$
0	87.90	0.4905	0.4905	0.3245	0.324
5	85.90	.4941	.4941	.3254	.325
10	83.95	.4979	.4979	.3262	.326
15	82.04	.5018	.5021	.3270	.3271
18	80.93	.5042	.5045	.3274	.327
20	80.18	.5059	.5064	.3277	.328
25	78.36	.5103	.5110	.3285	.329
30	76.58	.5148	.5159	.3294	.330
35	74.85	.5194	.5209	.3302	.331
38	73.83	.5223	.5241	.3307	.331
40	73.15	.5243	.5263	.3310	.332
45	71.50	.5293	.5319	.3318	.333
50	69.88	.5345	.5378	.3327	.334
55	68.30	.5400	.5439	.3335	.335
60	66.76	.5455	.5502	.3344	.337
65	65.25	.5514	.5568	.3353	.338
70	63.78	.5573	.5636	.3362	.340
75	62.34	.5635	.5707	.3371	.341
80	60.93	.5699	.5781	.3380	.342
85	59.55	.5766	.5859	.3389	.344
90	58.20	.5835	.5939	.3399	.345
95	56.88	.5906	.6022	.3409	.347
100	55.58	.5981	.6110	.3419	.349

[a] Values for the dielectric constant of water as determined by Owen et al. [12]: values above 70 °C we calculated from their equation expressing ϵ as a function of temperature.

The interionic distance parameter, $\mathring{a}_i$, is shown in Table 1-25 from the monograph by Garrels and Christ (1965, pp. 61, 62).

In Table 1-24, note the rather small variation in A and B, as a function of temperature. As an example, increasing the temperature from 15 to 25° changes A by only 1.7%, and B by only 0.05%. These variations are minimal, especially compared to the "uncertainty" in the choice of the "ionic diameter" ($\mathring{a}_i$ listed in Table 1-25). Recall in passing, however, that the activity coefficients themselves will vary exponentially with the listed values, but note that some "compensation" occurs as A and B enter the equation as a ratio (both increasing with temperature.)

Table 1-25

Values of $\mathring{a}_i$ for Some Individual Ions in Aqueous Solutions

$\mathring{a}_i \times 10^8$	Ion
2.5	Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+
3.0	K^+, Cl^-, Br^-, I^-, NO_3^-
3.5	OH^-, F^-, HS^-, BrO_3^-, IO_4^-, MnO_4^-
4.0–4.5	Na^+, HCO_3^-, $H_2PO_4^-$, HSO_3^-, Hg_2^{++}, SO_4^{--}, SeO_4^{--}, CrO_4^{--}, HPO_4^{--}, PO_4^{3-}
4.5	Pb^{++}, CO_3^{--}, SO_3^{--}, MoO_4^{--}
5.0	Sr^{++}, Ba^{++}, Ra^{++}, Cd^{++}, Hg^{++}, S^{--}, WO_4^{--}
6	Li^+, Ca^{++}, Cu^{++}, Zn^{++}, Sn^{++}, Mn^{++}, Fe^{++}, Ni^{++}, Co^{++}
8	Mg^{++}, Be^{++}
9	H^+, Al^{3+}, Cr^{3+}, trivalent rare earths
11	Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}

SOURCE: Adapted from I. M. Klotz, *Chemical Thermodynamics*. Englewood Cliffs, N.J., Prentice-Hall, 1950, p. 331.

The most extensive calculations of the theoretical mean activity coefficients (of strong electrolytes in aqueous solutions) have been presented by Hamer (1968). As these calculations represent the presently best available (theoretically calculated) data, several representative sets are quoted directly from the publication by Hamer. Thus, the following pages show the theoretical background on which the data have been calculated, and the actual values are shown in Table 1-27 through 1-32. The main point of interest in the present connection is to demonstrate that A) the (calculated) changes in the mean activity coefficients as a function of temperature are relatively minor, and B) that no "surprising", abrupt changes with temperature occur.

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Theoretical Expressions for Activity Coefficients

Activity coefficients give a measure of the deviations of real solutions from ideality and include the magnitude of all effects that lead to these deviations.

In dilute solutions the main effect is that of interionic attraction, i.e., the attraction between electrical (ionic) charges of unlike sign, and for which Debye and Hückel [3] assuming that ions are point charges derived a solution which led to the following expression for the mean activity coefficient, $\gamma_\pm$, of an electrolyte (γ shall be used hereafter for $\gamma_\pm$):

$$\log \gamma_c = -z_+z_-A_c\sqrt{I_c} \qquad (1)$$

where the subscript *c* refers to concentrations on the volume basis and

$$A_c = \left(\frac{2\pi N}{1000}\right)^{1/2} \frac{e^3}{2.302585k^{3/2}} \left(\frac{1}{T^{3/2}\epsilon^{3/2}}\right) = \frac{1.824829238 \times 10^6}{(T\epsilon)^{3/2}},$$

where the symbols have the following meanings and numerical values [4]:

N (or N_A) = Avogadro constant = $6.02252(28) \times 10^{23}$ mol^{-1}.

e = elementary charge (sometimes called the electronic or protonic charge) = 4.80298(20) esu.

k = Boltzmann constant = $1.38054(18) \times 10^{-16}$ erg K^{-1}.

T = absolute temperature in K (defined in the thermodynamic scale by assigning 273.16 K (Kelvin) to the triple point of water (freezing point of water, 273.15 K = 0 °C (Celsius). (The 13th General Conference on Weights and Measures in 1967 changed the unit of temperature and temperature interval from "degrees Kelvin" to simply "Kelvin," symbol: K.)

ϵ = dielectric constant of the solvent.

The values given in parentheses above represent established limits of error based on three standard deviations applied to the last digits in the listed value.

The following values of π and ln 10 were used in the calculations:

$$\pi = 3.14159265$$

$$\ln 10 = 2.302585$$

A_m on the molality (or weight) basis is given by $A_m = A_c(d_0)^{1/2}$ where d_0 is the density of the solvent. Values of ϵ, the dielectric constant, and of d_0, the density of water, from 0 to 100 °C, inclusive, are given in table 2 [5, 6]. Values of A_c and A_m for aqueous solutions from 0 to 100 °C, inclusive, are given in table 3.

Values of γ_c as calculated by equation (1) for 1-1, 1-2 (or 2-1), 1-3 (or 3-1), 1-4 (or 4-1 or 2-2), 2-3 (or 3-2), 2-4 (or 4-2), 3-3, 3-4 (or 4-3), and 4-4 electrolytes are given, respectively, in tables 4 to 12, inclusive, for ionic strengths of 0.1 and below and for temperatures from 0 to 100 °C, inclusive. Similar data for γ_m are given in tables 13 to 21, inclusive.

When the size, a_i, of the ions is taken into account, the Debye-Hückel equation becomes:

$$\log \gamma_c = \frac{-z_+z_-A_c\sqrt{I_c}}{1 + B_c a_i\sqrt{I_c}}$$

where

$$B_c = \left(\frac{8\pi N}{1000}\right)^{1/2} \frac{e}{k^{1/2}} \left(\frac{1}{T^{1/2}\epsilon^{1/2}}\right) = \frac{50.29158649 \times 10^8}{(T\epsilon)^{1/2}}$$

in which the symbols have the significances given above. B_m on the molality (or weight) basis is given by $B_m = B_c(d_0)^{1/2}$. Values of B_c and B_m for aqueous solutions from 0 to 100 °C, inclusive, are given in table 3.

Güntelberg [7] suggested the simpler form

$$\log \gamma_c = \frac{-z_+z_-A_c\sqrt{I_c}}{1 + \sqrt{I_c}} \qquad (2)$$

which is equivalent to assigning a value of approximately 3Å as calculated by equation (2) to the ion size at all temperatures. Güntelberg values of γ_c for 1-1, 1-2 (or 2-1), 1-3 (or 3-1), 1-4 (or 4-1 or 2-2), 2-3 (or 3-2), 2-4 (or 4-2), 3-3, 3-4 (or 4-3), and 4-4 electrolytes are given, respectively, in tables 22 to 30, inclusive, for ionic strengths of 0.1 and below and for temperatures from 0 to 100 °C, inclusive. Güntelberg values for γ_m for these same valence types and ranges of ionic strength and temperature are given in tables 31 to 39, inclusive.

A modified or extended Güntelberg equation would be

$$\log \gamma_c = \frac{-z_+z_-A_c\sqrt{I_c}}{1 + 3B_c\sqrt{I_c}} \qquad (3)$$

where the denominator is now temperature dependent since B_c is a function of temperature. Extended Güntelberg values of γ_c as calculated by equation (3) for 1-1, 1-2 (or 2-1), 1-3 (or 3-1), 1-4 (or 4-1 or 2-2), 2-3 (or 3-2), 2-4 (or 4-2), 3-3, 3-4 (or 4-3), and 4-4 electrolytes are given, respectively, in tables 40 to 48, inclusive, for ionic strengths of 0.1 and below and for temperatures from 0 to 100 °C, inclusive. Extended Güntelberg values for γ_m for the same valence types and ranges of ionic strength and temperature are given in tables 49 to 57, inclusive.

These Güntelberg expressions for the activity coefficient give a fair representation of a number of electrolytes up to $I = 0.1$. However, a better representation is obtained if a term linear in the ionic strength is added to the right side of the equations. Thus, Guggenheim [8] proposed the equation

$$\log \gamma_c = \frac{-z_+z_-A_c\sqrt{I_c}}{1 + \sqrt{I_c}} + bI_c$$

where b is an adjustable parameter.

Davies [9] altered the Guggenheim equation by putting $b = 0.2Az_+z_-$, thus:

$$\log \gamma_c = \frac{-z_+z_-A_c\sqrt{I_c}}{1+\sqrt{I_c}} + 0.2Az_+z_-I_c \qquad (4)$$

where the denominator of the first term on the right is again independent of temperature. Davies values of γ_c as calculated by equation (4) for 1-1, 1-2 (or 2-1), 1-3 (or 3-1), 1-4 (or 4-1 or 2-2), 2-3 (or 3-2), 2-4 (or 4-2), 3-3, 3-4 (or 4-3), and 4-4 electrolytes are given, respectively, in tables 58 to 66, inclusive, for ionic strengths of 0.1 and below and for temperatures from 0 to 100 °C, inclusive. Davies values for γ_m for the same valence types and ranges of ionic strength and temperature are given in tables 67 to 75, inclusive.

Scatchard [10] suggested that a better average fit is obtained if $(1 + 1.5\sqrt{I})$ is used in the denominator of the first term on the right for the expression for $\log \gamma_c$, thus:

$$\log \gamma_c = \frac{-z_+z_-A_c\sqrt{I_c}}{1+1.5\sqrt{I_c}} \qquad (5)$$

Scatchard actually used an additional linear term in I with an adjustable coefficient on the right side of the above equation but this additional term is omitted here. Scatchard values of γ_c as calculated by equation (5) for 1-1, 1-2 (or 2-1), 1-3 (or 3-1), 1-4 (or 4-1 or 2-2), 2-3 (or 3-2), 2-4 (or 4-2), 3-3, 3-4 (or 4-3), and 4-4 electrolytes are given, respectively, in tables 76 to 84, inclusive, for ionic strengths of 0.1 and below and for temperatures of 0 to 100 °C, inclusive. Scatchard values for γ_m for the same valence types and ranges of ionic strength and temperature are given in tables 85 to 93, inclusive.

A modified or extended Scatchard equation results if the denominator, $1 + 1.5\sqrt{I_c}$, in the above equation is made temperature dependent, thus:

$$\log \gamma_c = \frac{-z_+z_-A_c\sqrt{I_c}}{1+4.5B_c\sqrt{I_c}} \qquad (6)$$

Extended Scatchard values for γ_c as calculated by equation (6) for 1-1, 1-2 (or 2-1), 1-3 (or 3-1), 1-4 (or 4-1 or 2-2), 2-3 (or 3-2), 2-4 (or 4-2), 3-3, 3-4 (or 4-3), and 4-4 electrolytes are given, respectively, in tables 94 to 102, inclusive, for ionic strengths of 0.1 and below and for temperatures from 0 to 100 °C, inclusive. Extended Scatchard values for γ_m for the same valence types and ranges of ionic strength and temperature are given in tables 103 to 111, inclusive.

Bjerrum [11] has shown that ion pairs (associated ions with charges of unlike sign) occur if the diameter of the ion is less than

$$a_B = \frac{z_+z_-e^2}{2\epsilon kT}$$

Values of a_B for aqueous solutions from 0 to 100 °C, inclusive, are given in table 112. The Bjerrum expression for the activity coefficient is:

$$\log \gamma_c = \frac{-z_+z_-A_c\sqrt{I_c}}{1+B_ca_B\sqrt{I_c}} \qquad (7)$$

Bjerrum values of γ_c as calculated by equation (7) for 1-1, 1-2 (or 2-1), 1-3 (or 3-1), 1-4 (or 4-1 or 2-2), 2-3 (or 3-2), 2-4 (or 4-2), 3-3, 3-4 (or 4-3), and 4-4 electrolytes are given, respectively in tables 113 to 121, inclusive, for ionic strengths of 0.1 and below and for temperatures of 0 to 100 °C, inclusive. Bjerrum values for γ_m for the same valence types and ranges of ionic strength and temperature are given in tables 122 to 130, inclusive.

Table 1-26

Bjerrum's minimum ion-parameter for uni-univalent electrolytes in aqueous solutions from 0 to 100 °C based on the dielectric constant of water determined by Owen et al. [12].

Temperature	Ion-parameter	Temperature	Ion-parameter
t	a_B	t	a_B
°C	10^8 cm	°C	10^8 cm
(On weight or volume basis)			
0	*3.48(3.49)	50	3.70
5	3.50	55	3.73
10	3.52	60	3.76(3.75)
15	3.53(3.54)	65	3.79(3.78)
18	3.55	70	3.82(3.81)
20	3.56	76	3.85(3.84)
25	3.58	80	3.88
30	3.60	85	3.92(3.91)
35	3.62	90	3.95(3.94)
38	3.64	95	3.99(3.98)
40	3.65	100	4.03(4.02)
45	3.67		

Table 1-27

Mean activity coefficients of electrolytes in aqueous solutions on a volume basis – Debye-Hückel limiting law

(Electrolyte, z.z. = 1)

Ionic strength	Temperature in degrees Celsius											
	0	5	10	15	18	20	25	30	35	38	40	45
.0001	.9887	.9887	.9886	.9885	.9884	.9884	.9883	.9882	.9881	.9880	.9880	.9878
.0002	.9841	.9840	.9839	.9838	.9837	.9836	.9835	.9833	.9832	.9831	.9830	.9828
.0003	.9806	.9804	.9803	.9801	.9800	.9800	.9798	.9796	.9794	.9793	.9792	.9790
.0004	.9776	.9774	.9773	.9771	.9770	.9769	.9767	.9765	.9763	.9761	.9761	.9758
.0005	.9750	.9748	.9746	.9744	.9743	.9742	.9740	.9738	.9735	.9734	.9733	.9730
.0006	.9726	.9725	.9722	.9720	.9719	.9718	.9716	.9713	.9710	.9709	.9708	.9705
.0007	.9705	.9703	.9701	.9698	.9697	.9696	.9693	.9690	.9687	.9686	.9684	.9681
.0008	.9685	.9683	.9680	.9678	.9676	.9675	.9672	.9669	.9666	.9664	.9663	.9660
.0009	.9666	.9664	.9661	.9659	.9657	.9656	.9653	.9650	.9646	.9644	.9643	.9639
.0010	.9648	.9646	.9643	.9640	.9639	.9637	.9634	.9631	.9628	.9626	.9624	.9620
.0020	.9506	.9503	.9499	.9495	.9493	.9491	.9487	.9482	.9477	.9475	.9472	.9467
.0030	.9399	.9394	.9390	.9385	.9382	.9380	.9375	.9370	.9364	.9360	.9358	.9351
.0040	.9309	.9304	.9299	.9294	.9290	.9288	.9282	.9276	.9269	.9265	.9262	.9255
.0050	.9230	.9225	.9220	.9214	.9210	.9207	.9201	.9194	.9186	.9182	.9179	.9171
.0060	.9160	.9154	.9148	.9142	.9138	.9135	.9128	.9120	.9112	.9107	.9104	.9095
.0070	.9095	.9090	.9083	.9077	.9072	.9069	.9061	.9053	.9045	.9039	.9036	.9026
.0080	.9037	.9030	.9023	.9016	.9011	.9008	.9000	.8991	.8982	.8977	.8973	.8963
.0090	.8981	.8975	.8967	.8960	.8955	.8951	.8943	.8934	.8924	.8918	.8914	.8903
.0100	.8929	.8922	.8915	.8907	.8901	.8898	.8889	.8879	.8869	.8863	.8859	.8847
.0200	.8520	.8510	.8500	.8489	.8483	.8478	.8465	.8453	.8439	.8431	.8425	.8410
.0300	.8219	.8208	.8195	.8183	.8175	.8169	.8154	.8139	.8123	.8113	.8107	.8089
.0400	.7973	.7960	.7947	.7933	.7924	.7917	.7901	.7884	.7866	.7855	.7848	.7828
.0500	.7763	.7749	.7734	.7719	.7709	.7702	.7684	.7666	.7646	.7635	.7626	.7605
.0600	.7578	.7563	.7547	.7530	.7520	.7512	.7493	.7474	.7453	.7440	.7432	.7409
.0700	.7411	.7395	.7379	.7361	.7350	.7342	.7322	.7302	.7280	.7266	.7257	.7233
.0800	.7259	.7243	.7225	.7207	.7195	.7187	.7166	.7145	.7122	.7108	.7098	.7073
.0900	.7120	.7102	.7084	.7065	.7053	.7044	.7023	.7001	.6977	.6962	.6952	.6926
.1000	.6990	.6972	.6953	.6934	.6921	.6912	.6890	.6867	.6842	.6827	.6817	.6789

Table 1-28

Mean activity coefficients of electrolytes in aqueous solutions on a volume basis—Debye-Hückel limiting law

(Electrolyte, $z_+z_- = 2$)

Ionic strength	Temperature in degrees Celsius											
	0	5	10	15	18	20	25	30	35	38	40	45
.0001	.9776	.9774	.9773	.9771	.9770	.9769	.9767	.9765	.9763	.9761	.9761	.9758
.0002	.9685	.9683	.9680	.9678	.9676	.9675	.9672	.9669	.9666	.9664	.9663	.9660
.0003	.9615	.9613	.9610	.9607	.9605	.9604	.9600	.9597	.9593	.9590	.9589	.9585
.0004	.9557	.9554	.9551	.9547	.9545	.9544	.9540	.9536	.9531	.9529	.9527	.9522
.0005	.9506	.9503	.9499	.9495	.9493	.9491	.9487	.9482	.9477	.9475	.9472	.9467
.0006	.9460	.9457	.9453	.9449	.9446	.9444	.9439	.9434	.9429	.9426	.9424	.9418
.0007	.9418	.9414	.9410	.9406	.9403	.9401	.9396	.9390	.9385	.9381	.9379	.9373
.0008	.9379	.9375	.9371	.9366	.9363	.9361	.9355	.9350	.9344	.9340	.9337	.9331
.0009	.9343	.9339	.9334	.9329	.9326	.9323	.9318	.9312	.9305	.9301	.9299	.9292
.0010	.9309	.9304	.9299	.9294	.9290	.9288	.9282	.9276	.9269	.9265	.9262	.9255
.0020	.9037	.9030	.9023	.9016	.9011	.9008	.9000	.8991	.8982	.8977	.8973	.8963
.0030	.8833	.8826	.8817	.8809	.8803	.8799	.8789	.8779	.8768	.8761	.8757	.8745
.0040	.8665	.8657	.8647	.8637	.8631	.8627	.8616	.8604	.8592	.8584	.8579	.8565
.0050	.8520	.8510	.8500	.8489	.8483	.8478	.8465	.8453	.8439	.8431	.8425	.8410
.0060	.8391	.8380	.8369	.8358	.8350	.8345	.8332	.8318	.8303	.8295	.8288	.8272
.0070	.8274	.8263	.8251	.8239	.8231	.8225	.8211	.8196	.8181	.8171	.8165	.8147
.0080	.8166	.8155	.8142	.8129	.8121	.8115	.8100	.8085	.8068	.8058	.8051	.8033
.0090	.8067	.8054	.8041	.8028	.8019	.8012	.7997	.7981	.7964	.7953	.7946	.7927
.0100	.7973	.7960	.7947	.7933	.7924	.7917	.7901	.7884	.7866	.7855	.7848	.7828
.0200	.7259	.7243	.7225	.7207	.7195	.7187	.7166	.7145	.7122	.7108	.7098	.7073
.0300	.6755	.6736	.6716	.6696	.6682	.6673	.6649	.6625	.6599	.6583	.6572	.6543
.0400	.6357	.6337	.6315	.6293	.6278	.6268	.6243	.6216	.6188	.6170	.6159	.6127
.0500	.6026	.6005	.5982	.5958	.5943	.5932	.5905	.5877	.5847	.5829	.5816	.5783
.0600	.5742	.5719	.5696	.5671	.5655	.5643	.5615	.5586	.5555	.5536	.5523	.5489
.0700	.5492	.5469	.5444	.5419	.5402	.5390	.5362	.5332	.5299	.5280	.5266	.5231
.0800	.5270	.5246	.5221	.5194	.5177	.5165	.5136	.5105	.5072	.5052	.5038	.5002
.0900	.5069	.5045	.5019	.4992	.4975	.4962	.4932	.4901	.4867	.4847	.4833	.4796
.1000	.4885	.4861	.4835	.4808	.4790	.4778	.4747	.4715	.4681	.4661	.4647	.4610

Mean activity coefficients of electrolytes in aqueous solutions on a volume basis—Debye-Hückel limiting law—Continued

(Electrolyte, $z_+z_- = 2$)

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Table 1-29

Mean activity coefficients of electrolytes in aqueous solutions on a volume basis—Debye-Hückel limiting law

(Electrolyte, $z_+z_- = 4$)

Ionic strength	Temperature in degrees Celsius 0	5	10	15	18	20	25	30	35	38	40	45
.0001	.9557	.9554	.9551	.9547	.9545	.9544	.9540	.9536	.9531	.9529	.9527	.9522
.0002	.9379	.9375	.9371	.9366	.9363	.9361	.9355	.9350	.9344	.9340	.9337	.9331
.0003	.9245	.9240	.9235	.9229	.9225	.9223	.9216	.9210	.9202	.9198	.9195	.9187
.0004	.9134	.9128	.9122	.9115	.9111	.9108	.9101	.9093	.9085	.9080	.9076	.9067
.0005	.9037	.9030	.9023	.9016	.9011	.9008	.9000	.8991	.8982	.8977	.8973	.8963
.0006	.8950	.8943	.8935	.8927	.8922	.8919	.8910	.8901	.8891	.8885	.8880	.8869
.0007	.8871	.8863	.8855	.8847	.8841	.8837	.8828	.8818	.8807	.8801	.8796	.8785
.0008	.8797	.8789	.8781	.8772	.8766	.8762	.8752	.8742	.8730	.8724	.8719	.8706
.0009	.8729	.8721	.8712	.8703	.8697	.8692	.8682	.8671	.8659	.8652	.8647	.8633
.0010	.8665	.8657	.8647	.8637	.8631	.8627	.8616	.8604	.8592	.8584	.8579	.8565
.0020	.8166	.8155	.8142	.8129	.8121	.8115	.8100	.8085	.8068	.8058	.8051	.8033
.0030	.7803	.7789	.7775	.7759	.7749	.7742	.7725	.7707	.7688	.7676	.7668	.7647
.0040	.7509	.7494	.7478	.7461	.7450	.7442	.7423	.7403	.7382	.7369	.7360	.7336
.0050	.7259	.7243	.7225	.7207	.7195	.7187	.7166	.7145	.7122	.7108	.7098	.7073
.0060	.7041	.7023	.7005	.6985	.6973	.6964	.6942	.6919	.6895	.6880	.6870	.6843
.0070	.6846	.6827	.6808	.6787	.6774	.6765	.6742	.6718	.6692	.6677	.6666	.6638
.0080	.6669	.6650	.6629	.6608	.6595	.6585	.6561	.6536	.6509	.6493	.6482	.6453
.0090	.6507	.6487	.6466	.6444	.6430	.6420	.6395	.6370	.6342	.6325	.6314	.6283
.0100	.6357	.6337	.6315	.6293	.6278	.6268	.6243	.6216	.6188	.6170	.6159	.6127
.0200	.5270	.5246	.5221	.5194	.5177	.5165	.5136	.5105	.5072	.5052	.5038	.5002
.0300	.4563	.4538	.4511	.4483	.4465	.4452	.4421	.4389	.4354	.4333	.4319	.4281
.0400	.4042	.4016	.3988	.3960	.3942	.3929	.3897	.3864	.3829	.3808	.3793	.3755
.0500	.3632	.3606	.3578	.3550	.3531	.3518	.3487	.3454	.3418	.3397	.3383	.3345
.0600	.3297	.3271	.3244	.3216	.3198	.3185	.3153	.3121	.3086	.3065	.3050	.3013
.0700	.3017	.2991	.2964	.2936	.2918	.2906	.2875	.2843	.2808	.2788	.2773	.2737
.0800	.2777	.2752	.2725	.2698	.2680	.2668	.2637	.2606	.2572	.2552	.2538	.2502
.0900	.2569	.2545	.2519	.2492	.2475	.2462	.2433	.2402	.2369	.2349	.2336	.2301
.1000	.2387	.2363	.2338	.2311	.2295	.2283	.2254	.2224	.2191	.2172	.2159	.2125

[illegible] aqueous solutions on a volume basis—Debye-Huckel

Table 1-30

Mean activity coefficients of electrolytes in aqueous solutions on a weight basis—Extended Scatchard
(Electrolyte, z.z. = 1)

Ionic strength	Temperature in degrees Celsius											
	0	5	10	15	18	20	25	30	35	38	40	45
.0001	.9889	.9888	.9887	.9887	.9886	.9886	.9885	.9884	.9883	.9882	.9882	.9881
.0002	.9844	.9843	.9842	.9841	.9840	.9840	.9838	.9837	.9836	.9835	.9834	.9833
.0003	.9811	.9809	.9808	.9806	.9806	.9805	.9803	.9802	.9800	.9799	.9798	.9796
.0004	.9782	.9781	.9779	.9778	.9777	.9776	.9774	.9772	.9770	.9769	.9768	.9766
.0005	.9758	.9756	.9754	.9753	.9751	.9751	.9749	.9747	.9744	.9743	.9742	.9740
.0006	.9736	.9734	.9732	.9730	.9729	.9728	.9726	.9724	.9721	.9720	.9719	.9716
.0007	.9716	.9714	.9712	.9710	.9708	.9707	.9705	.9703	.9700	.9698	.9697	.9695
.0008	.9697	.9695	.9693	.9691	.9689	.9688	.9686	.9683	.9680	.9679	.9678	.9675
.0009	.9680	.9678	.9675	.9673	.9671	.9670	.9668	.9665	.9662	.9660	.9659	.9656
.0010	.9664	.9661	.9659	.9656	.9655	.9654	.9651	.9648	.9645	.9643	.9642	.9639
.0020	.9536	.9533	.9529	.9526	.9524	.9522	.9519	.9515	.9511	.9508	.9506	.9502
.0030	.9442	.9438	.9434	.9430	.9428	.9426	.9421	.9417	.9412	.9409	.9407	.9402
.0040	.9365	.9361	.9357	.9352	.9349	.9347	.9342	.9337	.9332	.9328	.9326	.9320
.0050	.9300	.9295	.9291	.9285	.9282	.9280	.9275	.9269	.9263	.9259	.9257	.9250
.0060	.9242	.9237	.9232	.9227	.9223	.9221	.9215	.9209	.9203	.9199	.9196	.9189
.0070	.9190	.9185	.9180	.9174	.9170	.9168	.9162	.9155	.9148	.9144	.9141	.9134
.0080	.9143	.9138	.9132	.9126	.9122	.9119	.9113	.9106	.9099	.9094	.9091	.9083
.0090	.9100	.9094	.9088	.9081	.9078	.9075	.9068	.9061	.9053	.9048	.9045	.9037
.0100	.9059	.9053	.9047	.9040	.9036	.9033	.9026	.9019	.9011	.9006	.9003	.8994
.0200	.8757	.8749	.8741	.8733	.8728	.8724	.8715	.8705	.8695	.8689	.8685	.8674
.0300	.8551	.8542	.8533	.8524	.8518	.8513	.8503	.8492	.8481	.8473	.8469	.8456
.0400	.8392	.8383	.8373	.8362	.8356	.8351	.8340	.8328	.8315	.8308	.8302	.8289
.0500	.8262	.8252	.8242	.8231	.8224	.8219	.8207	.8194	.8181	.8172	.8167	.8152
.0600	.8153	.8142	.8131	.8119	.8112	.8107	.8094	.8080	.8067	.8058	.8052	.8037
.0700	.8057	.8046	.8034	.8022	.8015	.8009	.7996	.7982	.7967	.7959	.7952	.7937
.0800	.7972	.7961	.7949	.7936	.7929	.7923	.7909	.7895	.7880	.7871	.7864	.7848
.0900	.7896	.7885	.7872	.7859	.7852	.7846	.7832	.7817	.7802	.7792	.7786	.7769
.1000	.7828	.7816	.7803	.7790	.7782	.7776	.7762	.7746	.7731	.7721	.7714	.7697

Mean activity coefficients of electrolytes in aqueous solutions on a weight basis—Extended Scatchard—Continued
(Electrolyte, z.z = 1)

Table 1-31

Mean activity coefficients of electrolytes in aqueous solutions on a weight basis—Extended
Scatchard
(Electrolyte, z.z. = 2)

Ionic strength	Temperature in degrees Celsius											
	0	5	10	15	18	20	25	30	35	38	40	45
.0001	.9779	.9778	.9776	.9774	.9773	.9773	.9771	.9769	.9767	.9766	.9765	.9763
.0002	.9691	.9689	.9687	.9684	.9683	.9682	.9679.	.9677	.9674	.9672	.9671	.9668
.0003	.9625	.9622	.9619	.9617	.9615	.9614	.9611	.9607	.9604	.9602	.9601	.9597
.0004	.9569	.9566	.9563	.9560	.9558	.9557	.9553	.9550	.9546	.9544	.9542	.9538
.0005	.9521	.9518	.9515	.9511	.9509	.9507	.9504	.9500	.9495	.9493	.9491	.9486
.0006	.9478	.9475	.9471	.9467	.9465	.9463	.9459	.9455	.9450	.9447	.9445	.9440
.0007	.9439	.9436	.9432	.9428	.9425	.9423	.9419	.9414	.9409	.9406	.9404	.9399
.0008	.9403	.9399	.9395	.9391	.9388	.9386	.9381	.9376	.9371	.9368	.9366	.9360
.0009	.9370	.9366	.9361	.9357	.9354	.9352	.9347	.9341	.9336	.9332	.9330	.9324
.0010	.9338	.9334	.9329	.9324	.9321	.9319	.9314	.9309	.9303	.9299	.9297	.9291
.0020	.9093	.9087	.9081	.9074	.9070	.9067	.9060	.9053	.9045	.9040	.9037	.9029
.0030	.8915	.8908	.8901	.8893	.8888	.8885	.8876	.8863	.8859	.8853	.8849	.8839
.0040	.8771	.8763	.8755	.8746	.8741	.8737	.8728	.8718	.8708	.8702	.8697	.8686
.0050	.8649	.8640	.8631	.8622	.8616	.8612	.8602	.8591	.8580	.8573	.8569	.8557
.0060	.8542	.8533	.8523	.8513	.8507	.8503	.8492	.8480	.8469	.8461	.8456	.8443
.0070	.8446	.8437	.8427	.8416	.8410	.8405	.8393	.8381	.8369	.8361	.8356	.8342
.0080	.8360	.8350	.8339	.8328	.8321	.8316	.8304	.8292	.8279	.8270	.8265	.8251
.0090	.8280	.8270	.8259	.8247	.8240	.8235	.8223	.8209	.8196	.8187	.8182	.8167
.0100	.8207	.8196	.8185	.8173	.8165	.8160	.8147	.8134	.8119	.8111	.8105	.8089
.0200	.7669	.7655	.7641	.7626	.7617	.7611	.7595	.7578	.7561	.7550	.7542	.7523
.0300	.7312	.7297	.7282	.7265	.7255	.7248	.7230	.7211	.7192	.7180	.7172	.7151
.0400	.7043	.7027	.7011	.6993	.6982	.6974	.6955	.6935	.6915	.6902	.6893	.6871
.0500	.6827	.6810	.6793	.6774	.6763	.6755	.6735	.6714	.6692	.6679	.6670	.6646
.0600	.6646	.6629	.6611	.6592	.6580	.6572	.6551	.6529	.6507	.6493	.6483	.6459
.0700	.6491	.6473	.6455	.6435	.6423	.6414	.6393	.6371	.6348	.6334	.6324	.6299
.0800	.6356	.6337	.6318	.6298	.6286	.6277	.6256	.6233	.6209	.6195	.6185	.6159
.0900	.6235	.6217	.6198	.6177	.6165	.6156	.6134	.6110	.6086	.6072	.6061	.6035
.1000	.6127	.6108	.6089	.6068	.6056	.6046	.6024	.6001	.5976	.5961	.5951	.5924

Mean activity coefficients of electrolytes in aqueous solutions on a weight basis—Extended

Table 1-32

Mean activity coefficients of electrolytes in aqueous solutions on a weight basis—Extended
Scatchard
(Electrolyte, z.z = 4)

Ionic strength	Temperature in degrees Celsius 0	5	10	15	18	20	25	30	35	38	40	45
.0001	.9563	.9560	.9557	.9554	.9552	.9551	.9547	.9543	.9539	.9537	.9535	.9531
.0002	.9392	.9388	.9383	.9379	.9376	.9374	.9369	.9364	.9359	.9355	.9353	.9347
.0003	.9263	.9258	.9253	.9248	.9245	.9242	.9236	.9230	.9224	.9220	.9217	.9210
.0004	.9157	.9152	.9146	.9140	.9136	.9133	.9127	.9120	.9112	.9108	.9105	.9097
.0005	.9066	.9060	.9053	.9046	.9042	.9039	.9032	.9024	.9016	.9011	.9008	.8999
.0006	.8984	.8977	.8970	.8963	.8959	.8955	.8948	.8939	.8931	.8925	.8921	.8912
.0007	.8910	.8903	.8896	.8888	.8883	.8880	.8871	.8862	.8853	.8847	.8843	.8833
.0008	.8842	.8835	.8827	.8819	.8814	.8810	.8801	.8792	.8782	.8776	.8772	.8761
.0009	.8779	.8771	.8763	.8754	.8749	.8745	.8736	.8726	.8716	.8709	.8705	.8694
.0010	.8720	.8712	.8704	.8694	.8689	.8685	.8675	.8665	.8654	.8648	.8643	.8631
.0020	.8268	.8257	.8246	.8234	.8227	.8222	.8209	.8196	.8182	.8173	.8167	.8152
.0030	.7948	.7935	.7922	.7908	.7900	.7894	.7879	.7864	.7847	.7837	.7831	.7813
.0040	.7693	.7679	.7665	.7650	.7641	.7634	.7618	.7601	.7583	.7572	.7565	.7545
.0050	.7480	.7466	.7450	.7434	.7424	.7417	.7400	.7381	.7362	.7350	.7342	.7322
.0060	.7297	.7281	.7265	.7247	.7237	.7229	.7211	.7192	.7172	.7159	.7151	.7129
.0070	.7134	.7118	.7101	.7083	.7072	.7064	.7045	.7025	.7004	.6991	.6982	.6959
.0080	.6989	.6972	.6954	.6935	.6924	.6916	.6896	.6875	.6853	.6840	.6831	.6807
.0090	.6856	.6839	.6821	.6802	.6790	.6782	.6761	.6740	.6717	.6703	.6694	.6670
.0100	.6735	.6717	.6699	.6679	.6667	.6659	.6638	.6615	.6592	.6578	.6569	.6544
.0200	.5881	.5860	.5839	.5816	.5802	.5792	.5768	.5743	.5716	.5700	.5689	.5660
.0300	.5347	.5325	.5302	.5278	.5264	.5253	.5227	.5200	.5172	.5155	.5143	.5113
.0400	.4961	.4938	.4915	.4830	.4875	.4864	.4838	.4810	.4781	.4761	.4752	.4721
.0500	.4661	.4638	.4614	.4589	.4574	.4563	.4536	.4508	.4479	.4461	.4449	.4417
.0600	.4417	.4394	.4370	.4345	.4330	.4319	.4292	.4263	.4234	.4216	.4204	.4172
.0700	.4214	.4190	.4167	.4141	.4126	.4115	.4083	.4059	.4030	.4012	.3999	.3968
.0800	.4040	.4016	.3992	.3967	.3952	.3940	.3913	.3885	.3856	.3838	.3825	.3794
.0900	.3888	.3865	.3841	.3815	.3800	.3789	.3762	.3734	.3704	.3686	.3674	.3643
.1000	.3755	.3731	.3708	.3682	.3667	.3656	.3629	.3601	.3572	.3554	.3541	.3510

Mean activity coefficients of electrolytes in aqueous solutions on a weight basis—Extended
Scatchard—Continued
(Electrolyte, z.z. = 4)

Thickness of the Ionic Atmosphere

Table 1-33 gives the thickness of the ionic atmosphere ($1/\kappa$; in Å) at different temperatures and concentrations for a number of electrolytes (uni-univalent, uni-divalent, etc). The Table is taken from the monograph by Falkenhagen (1971). Note that, as a rough approximation, the thickness of the ionic atmosphere is approximately equal to:

$$1/\kappa \approx 10^{-8}/\sqrt{c} \quad \text{(in cm.)}$$

As the concentration increases from 10^{-4} to 10^{-2} molar, the thickness of the ionic atmosphere decreases by a factor of 10.

Table 1-33

c in $\frac{mol}{l}$	Valence					
	1-1	1-2	2-2	1-3	1-4	2-4
t = 0°C; D_0 = 87.91						
10^{-4}	306.89	177.12	153.45	125.27	97.03	88.58
10^{-3}	97.03	56.03	48.53	39.62	30.69	28.01
10^{-2}	30.69	17.72	15.35	12.53	9.71	8.86
10^{-1}	9.71	5.60	4.85	3.99	3.07	2.80
t = 18°C; D_0 = 80.82						
10^{-4}	303.79	175.33	151.89	124.00	96.05	87.68
10^{-3}	96.05	55.46	48.04	39.22	30.38	27.73
10^{-2}	30.38	17.54	15.19	12.41	9.61	8.77
10^{-1}	9.61	5.55	4.80	3.93	3.04	2.77
t = 25°C; D_0 = 78.25						
10^{-4}	302.45	174.55	151.23	123.46	95.63	87.30
10^{-3}	95.63	55.22	47.82	39.05	30.24	27.61
10^{-2}	30.24	17.46	15.13	12.35	9.57	8.73
10^{-1}	9.57	5.52	4.78	3.91	3.03	2.76
t = 100°C; D_0 = 56.23						
10^{-4}	286.88	165.56	143.43	117.10	90.70	82.80
10^{-3}	90.91	52.37	45.36	37.04	28.69	26.19
10^{-2}	28.69	16.56	14.35	11.71	9.07	8.28
10^{-1}	9.09	5.24	4.53	3.71	2.87	2.62

The prefactor in many potentiometric expressions is given by:

$$k = 2.30258 \cdot \frac{RT}{F} \text{ (Absolute Volts)}$$

For the sake of convenience, this parameter has been tabulated in Table$^{1-34}$ (Ives and Janz, page 67, Table IV).

Table I-34

VALUES OF $k = 2.30258(RT/F)$ (ABSOLUTE VOLTS)

Temp., °C	k (references *102, 23*); ice-point = 273.16	k (reference *100*); ice-point = 273.150
0	0.054197	0.054195
5	0.055189	0.055187
10	0.056182	0.056179
15	0.057173	0.057171
18	0.057768	0.057766
20	0.058165	0.058163
25	0.059158	0.059155
30	0.060149	0.060147
35	0.061141	0.061139
40	0.062133	0.062131
45	0.063126	0.063123
50	0.064117	0.064115
55	0.065109	0.065107
60	0.066102	0.066099

A.2. Dissociation Constants

The effects of temperature on the dissociation constant of water are reflected in Table I-35; however, these data are, to a large extent, primarily of theoretical interest. Superimposed on the relatively small changes in pH, induced by the temperature effects on the dissociation equilibrium of water, must be added the generally far more significant effects of changes in carbon dioxide concentration which will significantly affect the pH. This problem is treated in the Section on CO_2 and carbonate solubility relations. Lee (1973) points out that water with an alkalinity of 3.4 milliequivalent/liter (in the form of calcium carbonate) has a pH of 8.0 at 0° temperature in equilibrium with a partial pressure of CO_2 of 0.25 millimeter Hg. Increasing the temperature of this water to 25° results in a change in the pH of this system from 8.0 to 8.76 (Lee and Delfino, 1969), rather than the decrease which would be predicted from the dissociation constants quoted in Table I-35.

Table I-35

Ionization Constant of Water, K_w

t °C	$K_w \times 10^{14}$
0	0.1139
5	0.1846
10	0.2920
15	0.4505
20	0.6809
25	1.008
30	1.469
35	2.089
40	2.919
45	4.018
50	5.474
55	7.297
60	9.614

Values for a number of ionization constants as functions of temperature are shown in Tables I-36, 37, 38, and 39. The Tables are all taken from the Monograph by Harned and Owen (1958). The first two Tables represent the more commonly encountered acids, including carbonic acid in water and in a number of sodium chloride solutions. Tables I-38 and I-39 give some ionization constants which may be of use in connection with the specific occurrence of organic compounds; these are generally present only in minute quantities in naturally-occurring water, except under circumstances where man-made pollution may be significant.

Table 1-36

OBSERVED IONIZATION CONSTANTS IN WATER.
ALL VALUES ARE ON THE m-SCALE

Acid	Solvent		0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
Carbonic	Water	$K_{1A} \times 10^{7}$	2.64	3.04	3.44	3.81	4.16	4.45	4.71	4.90	5.04	5.13	5.19
	0.1*M* NaCl	"	4.48	5.16	5.84	6.49	7.11	7.66	8.14	8.54	8.95	9.06	9.16
	0.2*M* NaCl	"	5.15	5.93	6.70	7.44	8.14	8.78	9.33	9.79	10.15	10.39	10.51
	0.5*M* NaCl	"	6.23	7.14	8.04	8.90	9.70	10.41	11.03	11.53	11.92	12.19	12.32
	0.7*M* NaCl	"	6.62	7.56	8.47	9.34	10.15	10.81	11.51	12.03	12.45	12.75	12.93
	1.0*M* NaCl	"	7.02	7.98	8.92	9.80	10.63	11.37	12.02	12.58	13.03	13.37	13.58
Phosphoric	Water	$K_{2A} \times 10^{8}$	4.85	5.24	5.57	5.89	6.12	6.34	6.46	6.53	6.58	6.60	6.55
Phenolsulphonic	"	$K_{2A} \times 10^{10}$	4.45	5.20	6.03	6.92	7.85	8.85	9.80	10.94	12.00	13.09	14.16
Glycine	"	$K_{1A} \times 10^{3}$	..	3.82	3.99	4.17	4.32	4.46	4.57	4.66	4.73	4.77	4.79
Benzoic	"	$K_{1A} \times 10^{4}$	....	....	....	....	6.24	6.29	6.27	6.24	....	....	....
Citric	"	$K_{1A} \times 10^{4}$	6.03	6.31	6.69	6.92	7.21	7.45	7.66	7.78	7.96	7.99	8.04
	"	$K_{2A} \times 10^{5}$	1.45	1.54	1.60	1.65	1.70	1.73	1.76	1.77	1.75	1.76	1.75
	"	$K_{3A} \times 10^{7}$	4.05	4.11	4.14	4.13	4.09	4.02	3.96	3.78	3.60	3.45	3.28

Table 1-37

OBSERVED IONIZATION CONSTANTS IN WATER. ALL VALUES ARE ON THE m-SCALE.

Acids		0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
Formic	$K_A \times 10^{4}$	1.638	1.691	1.728	1.749	1.765	1.772	1.768	1.747	1.716	1.685	1.650	1.607	1.551
Acetic	$K_A \times 10^{5}$	1.657	1.700	1.729	1.745	1.753	1.754	1.750	1.728	1.703	1.670	1.633	1.589	1.542
Propionic	$K_A \times 10^{5}$	1.274	1.305	1.326	1.336	1.338	1.336	1.326	1.310	1.280	1.257	1.229	1.195	1.160
n-Butyric	$K_A \times 10^{5}$	1.563	1.574	1.576	1.560	1.542	1.515	1.484	1.439	1.395	1.347	1.302	1.252	1.199
Chloro-acetic	$K_A \times 10^{3}$	1.528	....	1.488	1.440†	....	1.379	1.308‡		1.230	....	....	....	....
Lactic	$K_A \times 10^{4}$	1.287	....	1.361*	....	....	1.374	....	1.336**	....	....	1.270	....	....
Glycolic	$K_A \times 10^{4}$	1.334	....	1.427*	....	....	1.475	....	1.471**	....	....	1.415	....	....
Sulfuric	$K_{2A} \times 10^{2}$		1.80	....	1.36	....	1.01	....	0.75	....	0.56	....	0.41	....
Carbonic	$K_{2A} \times 10^{11}$	2.36	2.77	3.24	3.71	4.20	4.69	5.13	5.62	6.03	6.38	6.73	....	....
Oxalic	$K_{2A} \times 10^{5}$	5.91	5.82	5.70	5.55	5.40	5.18	4.92	4.67	4.41	4.09	3.83	....	....
Malonic	$K_{2A} \times 10^{6}$	2.140	2.165	2.182	2.121	2.076	2.014	1.948	1.863	1.768	1.670	1.575	1.469	1.362
Phosphoric	$K_{1A} \times 10^{3}$	8.968	....	8.304*	....	....	7.516	....	6.531**	....	....	5.495	....	....
	$K_{2A} \times 10^{8}$	....	....	....	....	6.056	6.229	6.340	6.430	6.471	6.475	6.439	....	....
Boric	$K_A \times 10^{10}$	....	3.63	4.17	4.72	5.25	5.79	6.34	6.86	7.38	....	8.32	....	....
Amino-Acids														
Glycine	$K_A \times 10^{3}$	....	....	3.94	....	4.31	4.47	4.60	....	4.81	....	....	....	....
	$K_B \times 10^{5}$	....	....	4.68	5.12	5.57	6.04	6.52	6.98	7.43	7.87	....	....	....
Alanine	$K_A \times 10^{3}$	....	....	....	....	4.47	4.57	4.66	4.71	4.74	4.76	....	....	....
	$K_B \times 10^{5}$	....	....	....	....	6.90	7.47	8.08	8.61	9.10	9.60	....	....	....

Table 1-38

OBSERVED IONIZATION CONSTANTS IN WATER.

		0°	10°	20°	25°	30°	40°	50°	60°
Ammonia	$K_B \times 10^5$	1.374	1.570	1.710	1.774	1.820	1.862	1.892	
Ethylene diammonium ion	$K_{1B} \times 10^8$	2.73	5.42	10.35	16.2	20.2	34.4	60.1	103.3
	$K_{2B} \times 10^{11}$	1.94	4.14	9.41	13.8	18.5	30.9	56.0	95.8
Hexamethylamine	$K_{1B} \times 10^{11}$	1.73	4.22	9.66	14.8	21.2	44.3	88.7	171.0
Diammonium ion	$K_{2B} \times 10^{10}$	1.20	3.40	7.85	11.7	17.3	36.2	73.0	141.9
Valeric acid	$K_{1A} \times 10^5$	1.504	1.501	1.463	1.436	1.409	1.329	1.241	1.147
Hexoic acid	$K_{1A} \times 10^5$	1.445	1.449	1.416	1.389	1.364	1.287	1.201	1.110
Iso-butyric acid	$K_{1A} \times 10^5$	1.497	1.489	1.447	1.417	1.387	1.301	1.203	1.110
Iso-valeric acid	$K_{1A} \times 10^5$	1.679	1.719	1.705	1.657	1.605	1.477	1.345	1.216
Iso-hexoic acid	$K_{1A} \times 10^5$	1.491	1.491	1.456	1.426	1.402	1.322	1.235	1.141
Trimethylacetic acid	$K_{1A} \times 10^5$	0.965	0.968	0.944	0.929	0.911	0.855	0.797	0.733
Diethyl acetic acid	$K_{1A} \times 10^5$	2.334	2.169	1.968	1.859	1.744	1.540	1.353	1.181

Table 1-39

OBSERVED IONIZATION CONSTANTS OF AMINO-ACIDS* IN WATER. ALL VALUES ARE ON THE m-SCALE

	1°	12.5°	25°	37.5°	50°
dl-Alanine, $K_A \times 10^3$	3.75	4.14	4.49	4.68	4.66
$K_B \times 10^5$	4.83	6.10	7.40	8.73	9.86
dl-α-Amino-n-butyric acid, $K_A \times 10^3$	4.63	4.90	5.18	5.15	5.05
$K_B \times 10^5$	4.25	5.50	6.81	8.22	9.38
dl-α-Amino-n-valeric acid, $K_A \times 10^3$	4.21	4.57	4.81	4.91	4.86
$K_B \times 10^5$	4.04	5.18	6.47	7.64	8.63
dl-Norleucine, $K_A \times 10^3$	4.04	4.41	4.62	4.74	4.70
$K_B \times 10^5$	4.41	5.62	6.87	8.05	9.16
α-Aminoisobutyric acid, $K_A \times 10^3$	3.81	4.17	4.40	4.46	4.41
$K_B \times 10^5$	1.14	1.38	1.61	1.84	1.99
dl-Valine, $K_A \times 10^3$	4.79	5.05	5.19	5.11	4.90
$K_B \times 10^5$	3.24	4.21	5.27	6.28	7.28
dl-Leucine, $K_A \times 10^3$	4.14	4.49	4.70	4.71	4.65
$K_B \times 10^5$	3.57	4.52	5.60	6.71	7.59
dl-Isoleucine, $K_A \times 10^3$	4.32	4.59	4.81	4.82	4.66
$K_B \times 10^5$	3.61	4.57	5.77	6.79	7.85

A.3. Osmotic Pressure

In Table I-40, 41, and 42, are listed, respectively, the osmotic pressures of seawater for various salinities, at the respective freezing points.

Table I-41 shows the vapor pressure and the osmotic equivalent of seawater at 25°, as a function of chlorinity (in ppt) at 25°. As is to be expected, to a fair approximation, the osmotic pressure increases nearly linearly with the chlorinity over the limited range indicated.

Table I-42 gives the osmotic pressure in atmospheres of seasalt solutions as a function of concentration (in weight percent of salts), at a few temperatures. At the lower concentrations, the osmotic pressure is again seen to increase roughly linearly with concentration. The increase in the osmotic pressure with increasing temperature is essentially proportional to the ratios of the temperatures (in °K).

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Table 1-40

Freezing point and osmotic pressure of sea water at various salinities (After DEFANT, 1961)

Salinity (‰)	5	10	15	20	25	30	35	40
Freezing point (°C)	−0·267	−0·534	−0·802	−1·074	−1·349	−1·627	−1·910	−2·196
Osmotic pressure (atm)	3·23	6·44	9·69	12·98	16·32	19·67	23·12	26·59

Table 1-41

Vapor Pressure and Osmotic Equivalent of Seawater at 25°C
(From R. A. Robinson *J. Marine Biol. Assoc. U.K.*, 33, 449 (1954), with permission of Marine Biological Association of the United Kingdom)[a]

Cl, ‰	*R*	NaCl	KCl	$CaCl_2$	$MgCl_2$	$MgSO_4$	Na_2SO_4	Sucrose	Urea	V.P. Lowering[b]	Osmotic Pressure, atm
10	0.02861	0.2661	0.2908	0.2039	0.2005	0.5056	0.2374	0.5065	0.5400	0.00946	12.87
11	0.02869	0.3156	0.3211	0.2240	0.2199	0.5597	0.2643	0.5560	0.5965	0.01042	14.19
12	0.02877	0.3452	0.3516	0.2441	0.2393	0.6138	0.2918	0.6053	0.6534	0.01139	15.51
13	0.02885	0.3751	0.3825	0.2642	0.2588	0.6675	0.3196	0.6546	0.7112	0.01237	16.85
14	0.02893	0.4050	0.4134	0.2481	0.2780	0.7206	0.3477	0.7040	0.7695	0.01334	18.19
15	0.02901	0.4352	0.4447	0.3043	0.2975	0.7738	0.3762	0.7534	0.8285	0.01433	19.55
16	0.02908	0.4653	0.4760	0.3243	0.3165	0.8264	0.4051	0.8025	0.8860	0.01532	20.91
17	0.02916	0.4957	0.5077	0.3445	0.3356	0.8786	0.4347	0.8516	0.9462	0.01631	22.28
18	0.02924	0.5263	0.5397	0.3645	0.3546	0.9300	0.4648	0.9006	1.010	0.01732	23.66
19	0.02932	0.5571	0.5719	0.3845	0.3738	0.9803	0.4954	0.9497	1.071	0.01833	25.06
20	0.02940	0.5880	0.6043	0.4044	0.3929	1.028	0.5264	0.9982	1.133	0.01936	26.47
21	0.02948	0.6191	0.6370	0.4243	0.4122	1.076	0.5576	1.047	1.197	0.02039	27.89
22	0.02956	0.6503	0.6698	0.4440	0.4313	1.123	0.5896	1.095	1.260	0.02142	29.33

[a] This column gives the relative pressure lowering $\Delta p/p^0 = (p^0 - p)/p^0$, where p is the vapor pressure of seawater and p^0 is the vapor pressure of pure water. $p^0 = 23.756$ mm at 25°C.

[b] A. B. Arons and C. F. Kientzler, *Trans. Am. Geophys. Union*, 35, 722 (1954), also give vapor pressure information for sea salt solutions.

Table 1-42

Osmotic Pressure (in atm) of Sea Salt Solutions
(From R. W. Stoughton and M. H. Lietzke, *J. Chem. Eng. Data*, **12**, 101 (1967), with permission of American Chemical Society)

	Wt % Salts								
T, °C	1.00	2.00	3.45[a]	5.00	7.50	10.00	15.00	20.00	25.00
25	7.11	14.29	25.15	37.49	59.30	83.97	144.93	228.59	348
40	7.42	14.93	26.34	39.35	62.41	88.53	152.81	239.86	362
60	7.80	15.70	27.74	41.51	65.98	94.69	161.53	252.06	376
80	8.13	16.37	28.94	43.32	68.69	97.82	168.27	261.17	386
100	8.42	16.94	29.92	44.79	71.17	100.97	173.16	267.47	393

A.4. pH and pε Relationships

In natural waters, the pH is determined primarily by CO_2 in equilibrium with various carbonates. Silicates also play a role in the buffering of naturally-occurring waters. In Tables I-43, & I-44 are outlined some of the more important equations used for calculating pH and buffering of natural waters.

Table I-43 also includes some of the more important expressions for determining redox potentials.

For a detailed discussion of pH, buffering and redox potentials,, particularly of sediments, see the standard treatises by Pourbaix (1949), Garrels and Christ (1965), Horne (1969) or Stumm and Morgan (1970).

Table I-43

pH and pϵ

$pH = -\log\{H^+\}$		$p\epsilon = -\log\{e\}$	
Acid–base reaction: $HA + H_2O = H_3O^+ + A^-$; K_1	(1*a*)	Redox reaction: $Fe^{3+} + \frac{1}{2}H_2(g) = Fe^{2+} + H^+$; K_1	(1*b*)
Reaction (1*a*) is composed of two steps:		Reaction (1*b*) is composed of two steps:	
$HA = H^+ + A^-$; K_2	(2*a*)	$Fe^{3+} + e = Fe^{2+}$; K_2	(2*b*)
$H_2O + H^+ = H_3O^+$; K_3	(3*a*)	$\frac{1}{2}H_2(g) = H^+ + e$; K_3	(3*b*)
According to thermodynamic convention: $K_3 = 1$		According to thermodynamic convention: $K_3 = 1$	
Thus: $K_1 = K_2 = K_2K_3 = \{H^+\}\{A^-\}/\{HA\}$	(4*a*)	Thus: $K_1 = K_2 = K_2K_3 = \{Fe^{2+}\}/\{Fe^{3+}\}\{e\}$	(4*b*)
or $pH = pK + \log[\{A^-\}/\{HA\}]$	(5*a*)	or $p\epsilon = p\epsilon^\circ + \log[\{Fe^{3+}\}/\{Fe^{2+}\}]$	(5*b*)
Since $pK = -\log K = \Delta G^\circ/2.3RT$		Since $p\epsilon^\circ = \log K = -\Delta G^\circ/2.3RT$	
$pH = \Delta G^\circ/2.3RT + \log[\{A^-\}/\{HA\}]$	(6*a*)	$p\epsilon = -\Delta G^\circ/2.3RT + \log[\{Fe^{3+}\}/\{Fe^{2+}\}]$	(6*b*)
or for the transfer of 1 mole of H^+ from acid to H_2O:		or for the transfer of 1 mole of *e* to oxidant from H_2:	
$\Delta G/2.3RT = \Delta G^\circ/2.3RT + \log[\{A^-\}/\{HA\}]$	(7*a*)	$-\Delta G/2.3RT = -\Delta G^\circ/2.3RT + \log[\{Fe^{3+}\}/\{Fe^{2+}\}]$	(7*b*)
For the general case where *n* protons are transferred:		For the general case where *n* electrons are transferred:	
$H_nB + nH_2O = nH_3O^+ + B^{-n}$; β°	(8*a*)	$ox + (n/2)H_2 = red + nH^+$; $ox + ne = red$; K°	(8*b*)
$pH = (1/n)p\beta^\circ + (1/n)\log[\{B^{-n}\}/\{H_nB\}]$	(9*a*)	$p\epsilon = (1/n)\log K^\circ + (1/n)\log[\{ox\}/\{red\}]$;	
$pH = \Delta G/n2.3RT$		$p\epsilon = p\epsilon^\circ + (1/n)\log[\{ox\}/\{red\}]$	(9*b*)
$= \Delta G^\circ/n2.3RT + (1/n)\log[\{B^{-n}\}/\{H_nB\}]$	(10*a*)	$p\epsilon = -\Delta G^\circ/n2.3RT + (1/n)\log[\{ox\}/\{red\}]$	(10*b*)
$\Delta G = -nFE$ (E = acidity potential)	(11*a*)	$\Delta G = -nFE_H$ (E_H = redox potential)	(11*b*)
$pH = -E/(2.3RTF^{-1})$		$p\epsilon = E_H/(2.3RTF^{-1})$	
$= -E^\circ/(2.3RTF^{-1}) + (1/n)\log[\{B^{-n}\}/\{H_nB\}]$	(12*a*)†	$= E^\circ/2.3RTF^{-1} + (1/n)\log[\{ox\}/\{red\}]$	(12*b*)†
Acidity potential:		Redox potential (Peters-Nernst equation):	
$E = E^\circ + (2.3RT/nF)\log[\{H_nB\}/\{B^{-n}\}]$	(13*a*)	$E_H = E_H^\circ + (2.3RT/nF)\log[\{ox\}/\{red\}]$	(13*b*)

† At 25°C, $2.3RTF^{-1} = 0.059$ (V/eq). From (10) and (12): 25°C, $p\epsilon = E/0.059$, $p\epsilon^\circ = E_H^\circ/0.059$.

Most frequently used equations for calculating pH and pϵ (Stumm and Morgan, 1970, page 304).

Table I-44

Buffering of Aqueous Carbonate System

Titration Curve		Buffer Intensity	
I. C_T = constant Addition of strong acid or base:			
$C_B - C_A = C_T(\alpha_1 + 2\alpha_2) + [OH^-] - [H^+]$ $dC_B = d[\text{Alk}]$	(1)	$\frac{d[\text{Alk}]}{dpH} = \beta_{C_T}^{C_B} = 2.3\{C_T[\alpha_1(\alpha_0 + \alpha_2) + 4\alpha_2\alpha_0] + [H^+] + [OH^-]\}$	(2)
		$\beta_{C_T}^{C_B} \approx 2.3\alpha_1(\alpha_0 + \alpha_2)C_T$	(3)
II. [Alk] = constant Addition or removal of CO_2:			
$C_T = ([\text{Alk}] - [OH^-] + [H^+])/(\alpha_1 + 2\alpha_2)$ $dC_T = \frac{1}{2}d[\text{Acy}]$	(4)	$\frac{d[\text{Acy}]}{dpH} = \beta_{\text{Alk}}^{C_T} \simeq -4.6\frac{\alpha_1\alpha_0 + \alpha_1\alpha_2 + 4\alpha_2\alpha_0}{(\alpha_1 + 2\alpha_2)^2}[\text{Alk}]$	(5)
		$\beta_{\text{Alk}}^{C_T} \approx -4.6[(\alpha_0 + \alpha_2)/\alpha_1][\text{Alk}]$	(6)
III. [Acy] = constant Addition or removal of $NaCO_3/CaCO_3$			
$C_T = ([\text{Acy}] - [H^+] + [OH^-])/(\alpha_1 + 2\alpha_0)$ $dC_T = \frac{1}{2}d[\text{Alk}]$	(7)	$\frac{d[\text{Alk}]}{dpH} = \beta_{\text{Acy}}^{C_T} \simeq 4.6\frac{\alpha_1\alpha_0 + \alpha_1\alpha_2 + 4\alpha_2\alpha_0}{(\alpha_1 + 2\alpha_0)^2}[\text{Acy}]$	(8)
		$\beta_{\text{Acy}}^{C_T} \approx 4.6[(\alpha_0 + \alpha_2)/\alpha_1][\text{Acy}]$	(9)
IV. p_{CO_2} = constant Addition of strong base or strong acid:			
$C_B - C_A = (K_H(\alpha_1 + 2\alpha_2)/\alpha_0)p_{CO_2} + [OH^-] - [H^+]$ $dC_B = d[\text{Alk}]$	(10)	$\frac{d[\text{Alk}]}{dpH} = \beta_{p_{CO_2}}^{C_B} = 2.3\left\{K_H p_{CO_2}\frac{\alpha_1(\alpha_0 + \alpha_2) + 4\alpha_2\alpha_0 + (\alpha_1 + 2\alpha_2)^2}{\alpha_0} + [H^+] + [OH^-]\right\}$	(11)
		$\beta_{p_{CO_2}}^{C_B} \approx 2.3K_H p_{CO_2}/\alpha_0 \approx 2.3C_T$	(12)

Principle equations for evaluating buffering capacity of aqueous carbonate systems (Stumm and Morgan, 1970, page 138).

B.1 Solubility of Oxygen

An extensive discussion of the problem of the solubility of oxygen in natural waters is presented in Vol. I of the treatise by Hutchinson on Limnology. See also the recent data by Carpenter (1966) on the solubility of oxygen in pure water and natural waters. Table 1-47 shows the smoothed data for the oxygen solubility in saline waters of varying chlorinity (0.0 to 20.0 ‰) for 20.94% atmosphere oxygen at 100% relative humidity.

Other solubility data for oxygen as a function of chlorinity and temperature have been reported by Green and Carritt (1967). One of the interesting results by these authors is the observation that while the solubility of oxygen in seawater decreases essentially exponentially with concentration, the salting out was observed to decrease with increasing temperature, contrary to the predictions by the Debye theory.

Although the problems associated with determining accurately the solubilities of gases in water are not inconsiderable, at least the problem belongs in the realm of standard classical physical chemistry and is amenable to straightforward experimentation, the accuracy and precision of which can usually be improved by sheer preseverance. Far more difficult is the problem of rates of approach to various equilibria, particularly in solubility phenomena. Hutchinson has reviewed briefly some of the known aspects of the rate of changes in oxygen concentration. Relatively little has been done on the effects of temperature on this process. The reader is referred to the data by Adeney and Becker (reported by Hutchinson [1957] loco cit., p. 589).

Table 1-45

SOLUBILITY OF OXYGEN IN WATER

Some early determinations give slightly high values at lower temperatures (see Bohr and Bock, below). Recent determinations indicate that the lower values are probably correct (Morrison and Billet, also table following)

β = ml O_2 (at S.T.P.) absorbed by 1 ml H_2O at a pressure of O_2 of 1 atm.

	β				β		
t°	Winkler 1891	Morrison and Billet 1952	Bohr & Bock 1891	t°	Winkler 1891	Morrison and Billet 1952	Bohr & Bock 1891
0	0.0489	-	0.0496	40	0.0231	0.0232	0.0233
5	0.0429	-	0.439	50	0.0209	0.0208	0.207
10	0.0380	-	0.390	60	0.0195	0.0196	0.189
15	0.0342	0.0341	0.350	70	0.0183	0.0186	0.178
20	0.0310	0.0308	0.317	80	0.0176	0.0177	0.172
25	0.0283	0.0284	0.290	90	0.0172	-	0.169
30	0.0261	0.0265	0.268	100	0.0170	-	0.168

SOLUBILITY OF OXYGEN IN WATER IN CONTACT WITH AIR

These results, of considerable commercial and biological importance have been measured directly and calculated from data on pure oxygen. Morgan and Richardson, 1930 found that the values obtained in these two ways are the same. Extensive data upon the rate of solution of atmospheric oxygen and nitrogen in water are given in a series of papers by Adeney and Becker 1916-1920, 1919, 1920 and 1921.

Recent data again tend toward lower solubility values (see also table above). The following table was compiled by Truesdale, Downing and Lowden, 1955 for comparison of the various results these authors found the solubility at one atmosphere pressure (air and water vapor) to be: C = 14.161-0.3943t + 0.007714t²-0.0000646t³ where C is the concentration of oxygen in water in parts per million, and t is °C.

t°	Fox 1909	Winkler 1889[a]	Winkler 1891[b]	Roscoe & Lunt 1889	Jacobsen 1905[c]	Bohr & Bock, 1891	Royal Comm. 1908[d]	Truesdale, Downing and Lowden [illegible], 1955
0	14.65	14.56	14.55	-	14.30	14.79	-	14.16
5	12.80	12.72	12.73	12.41	12.48	13.07	-	12.37
10	11.33	11.27	11.24	11.11	11.01	11.58	11.11	10.92
15	10.15	10.09	10.06	9.98	9.85	10.32	9.94	9.76
20	9.17	9.10	9.10	8.96	8.91	9.30	8.60	8.84
25	8.38	8.24	8.24	8.25	8.16	8.46	8.12	8.11
30	7.63	7.53	7.52	-	-	7.71	-	7.53
35	7.10	-	-	-	-	7.04	-	7.04

[a]Titrametric analysis [b]Gasometric [c]As quoted by Fox, 1909 [d]Royal Commission on [illegible] [illegible] 5th Report, [illegible] Appendix 6, Part [illegible]

Table I-46

*Solubility of oxygen, from a wet atmosphere at a pressure of 760 mm. Hg, in mg. per liter, at temperatures from 0° to 35° C.**

Temp.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	14.16	14.12	14.08	14.04	14.00	13.97	13.93	13.89	13.85	13.81
1	13.77	13.74	13.70	13.66	13.63	13.59	13.55	13.51	13.48	13.44
2	13.40	13.37	13.33	13.30	13.26	13.22	13.19	13.15	13.12	13.08
3	13.05	13.01	12.98	12.94	12.91	12.87	12.84	12.81	12.77	12.74
4	12.70	12.67	12.64	12.60	12.57	12.54	12.51	12.47	12.44	12.41
5	12.37	12.34	12.31	12.28	12.25	12.22	12.18	12.15	12.12	12.09
6	12.06	12.03	12.00	11.97	11.94	11.91	11.88	11.85	11.82	11.79
7	11.76	11.73	11.70	11.67	11.64	11.61	11.58	11.55	11.52	11.50
8	11.47	11.44	11.41	11.38	11.36	11.33	11.30	11.27	11.25	11.22
9	11.19	11.16	11.14	11.11	11.08	11.06	11.03	11.00	10.98	10.95
10	10.92	10.90	10.87	10.85	10.82	10.80	10.77	10.75	10.72	10.70
11	10.67	10.65	10.62	10.60	10.57	10.55	10.53	10.50	10.48	10.45
12	10.43	10.40	10.38	10.36	10.34	10.31	10.29	10.27	10.24	10.22
13	10.20	10.17	10.15	10.13	10.11	10.09	10.06	10.04	10.02	10.00
14	9.98	9.95	9.93	9.91	9.89	9.87	9.85	9.83	9.81	9.78
15	9.76	9.74	9.72	9.70	9.68	9.66	9.64	9.62	9.60	9.58
16	9.56	9.54	9.52	9.50	9.48	9.46	9.45	9.43	9.41	9.39
17	9.37	9.35	9.33	9.31	9.30	9.28	9.26	9.24	9.22	9.20
18	9.18	9.17	9.15	9.13	9.12	9.10	9.08	9.06	9.04	9.03
19	9.01	8.99	8.98	8.96	8.94	8.93	8.91	8.89	8.88	8.86
20	8.84	8.83	8.81	8.79	8.78	8.76	8.75	8.73	8.71	8.70
21	8.68	8.67	8.65	8.64	8.62	8.61	8.59	8.58	8.56	8.55
22	8.53	8.52	8.50	8.49	8.47	8.46	8.44	8.43	8.41	8.40
23	8.38	8.37	8.36	8.34	8.33	8.32	8.30	8.29	8.27	8.26
24	8.25	8.23	8.22	8.21	8.19	8.18	8.17	8.15	8.14	8.13
25	8.11	8.10	8.09	8.07	8.06	8.05	8.04	8.02	8.01	8.00
26	7.99	7.97	7.96	7.95	7.94	7.92	7.91	7.90	7.89	7.88
27	7.86	7.85	7.84	7.83	7.82	7.81	7.79	7.78	7.77	7.76
28	7.75	7.74	7.72	7.71	7.70	7.69	7.68	7.67	7.66	7.65
29	7.64	7.62	7.61	7.60	7.59	7.58	7.57	7.56	7.55	7.54
30	7.53	7.52	7.51	7.50	7.48	7.47	7.46	7.45	7.44	7.43
31	7.42	7.41	7.40	7.39	7.38	7.37	7.36	7.35	7.34	7.33
32	7.32	7.31	7.30	7.29	7.28	7.27	7.26	7.25	7.24	7.23
33	7.22	7.21	7.20	7.20	7.19	7.18	7.17	7.16	7.15	7.14
34	7.13	7.12	7.11	7.10	7.09	7.08	7.07	7.06	7.05	7.05
35	7.04	7.03	7.02	7.01	7.00	6.99	6.98	6.97	6.96	6.95

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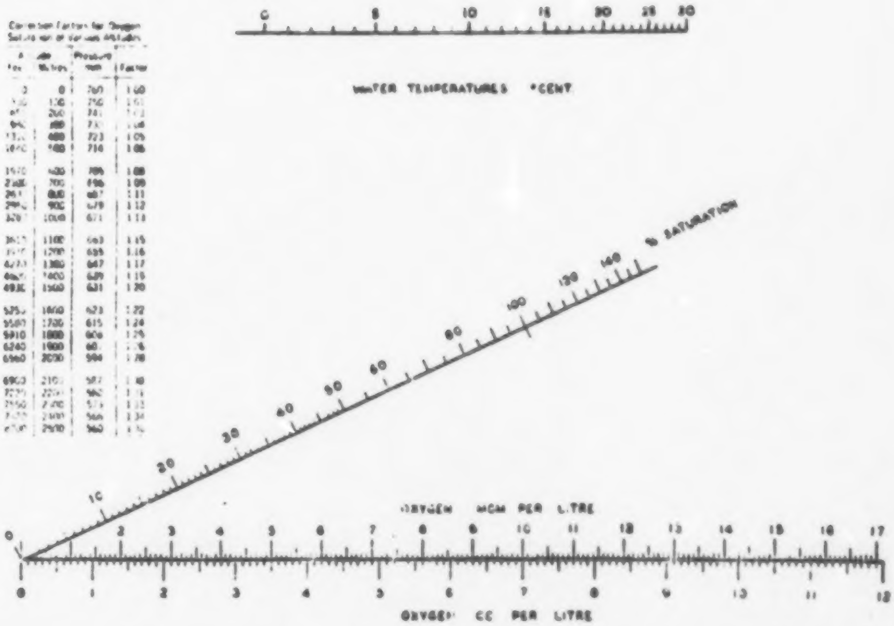
* From Truesdale, Downing, and Lowden (1955).

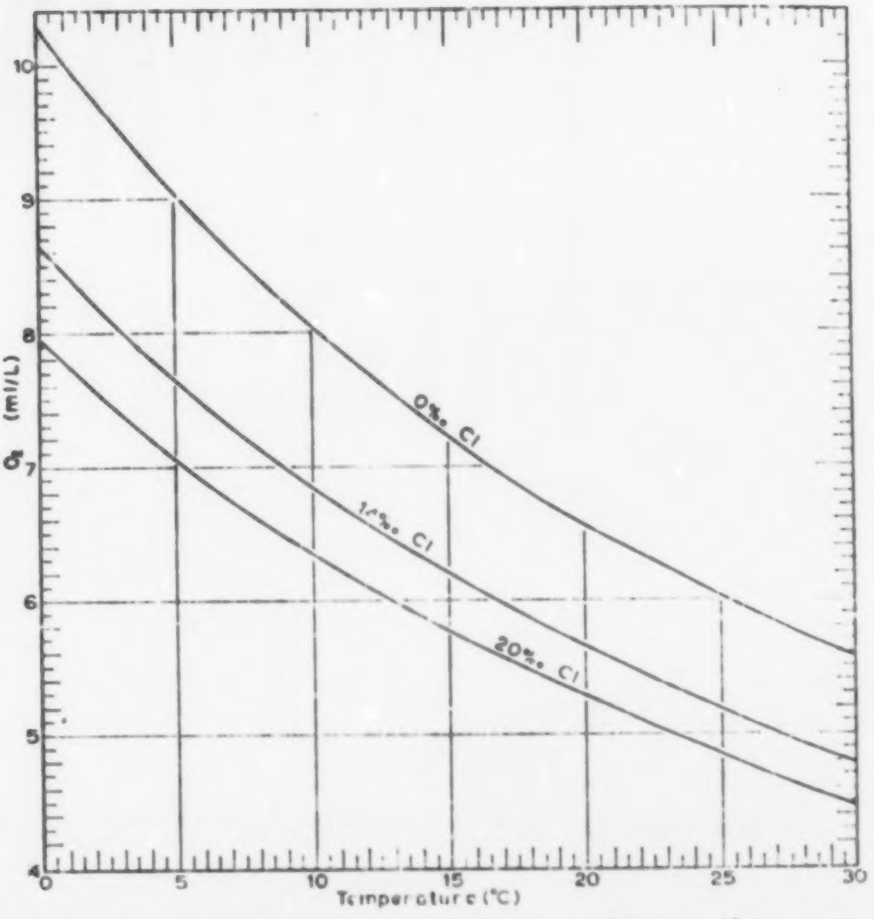


Correction Factors for Oxygen Saturation at Various Altitudes

Altitude Feet	Altitude Metres	Pressure mm	Factor
0	0	760	1.00
330	100	750	1.01
655	200	741	1.03
980	300	732	1.04
1310	400	723	1.05
1640	500	714	1.06
1970	600	705	1.08
2300	700	696	1.09
2610	800	687	1.11
2950	900	679	1.12
3280	1000	671	1.13
3610	1100	663	1.15
3940	1200	655	1.16
4270	1300	647	1.17
4600	1400	639	1.19
4930	1500	631	1.20
5250	1600	623	1.22
5580	1700	615	1.24
5910	1800	608	1.25
6240	1900	601	1.26
6560	2000	594	1.28
6900	2100	587	1.30
7220	2200	580	1.31
7550	2300	573	1.33
7880	2400	566	1.34
8200	2500	560	1.36

Nomogram for determining O_2 saturation at different temperatures and altitudes (Mortimer).

Figure 1-15



Dissolved oxygen values at selected chlorinities as they vary with temperature. (Drawn from data of Fox as given by Richards, 1965.)

Figure 1-16

Table I-47

Interpolated values of oxygen solubility (µg-at./liter) from an atmosphere of 20.94% O_2 and 100% relative humidity

Temp (°C)	Chlorinity (‰) 0.0	2.0	4.0	6.0	8.0	10.0	12.0	14.0	16.0	18.0	20.0
0.5	892	870	857	835	814	794	774	756	737	720	703
1.0	890	867	848	825	804	785	765	747	729	711	694
2.0	864	844	823	804	784	765	747	729	711	694	677
3.0	840	821	802	783	764	746	728	711	694	677	660
4.0	817	799	780	762	745	727	710	693	677	660	644
5.0	796	778	760	743	725	709	692	676	660	644	629
6.0	775	758	741	724	707	691	675	659	644	629	614
7.0	756	739	722	706	690	674	659	643	629	614	600
8.0	737	721	704	689	673	658	643	628	614	600	586
9.0	720	704	688	672	657	642	628	614	600	586	573
10.0	703	688	672	657	642	627	613	600	586	573	561
11.0	688	672	657	642	627	613	600	586	573	561	549
12.0	674	658	643	628	614	600	586	573	561	549	537
13.0	659	644	629	614	600	587	574	561	549	537	526
14.0	645	630	616	601	588	574	562	549	536	526	515
15.0	631	617	603	589	576	563	550	538	527	516	505
16.0	618	603	590	577	564	551	539	528	516	506	495
17.0	604	591	578	565	553	540	529	517	507	496	486
18.0	591	578	566	554	542	530	519	508	497	487	477
19.0	579	567	555	543	531	520	509	498	488	478	468
20.0	568	556	544	532	521	510	499	489	479	469	460
21.0	556	545	533	522	511	500	490	480	470	461	452
22.0	546	534	523	512	501	491	481	471	462	453	444
23.0	535	524	513	502	492	482	472	463	454	445	436
24.0	525	514	504	493	483	473	464	455	446	437	429
25.0	516	505	494	484	474	465	455	447	438	430	421
26.0	506	496	485	475	466	457	447	439	430	422	414
27.0	497	487	477	467	458	448	440	431	423	415	407
28.0	488	478	468	459	450	441	432	424	415	408	400
29.0	480	470	460	451	442	433	425	416	408	401	393
30.0	471	462	453	443	435	426	418	410	402	394	387
31.0	464	454	445	436	427	419	411	403	395	388	381
32.0	456	447	438	429	420	412	404	396	390	382	375
33.0	448	439	430	422	414	406	398	390	383	376	369
34.0	441	432	423	415	407	399	391	384	377	370	363
35.0	433	425	417	408	400	393	385	378	371	364	358
36.0	426	418	410	402	394	387	379	372	365	359	352

Oxygen Solubility Data as a Function of Temperature and Chlorinity.

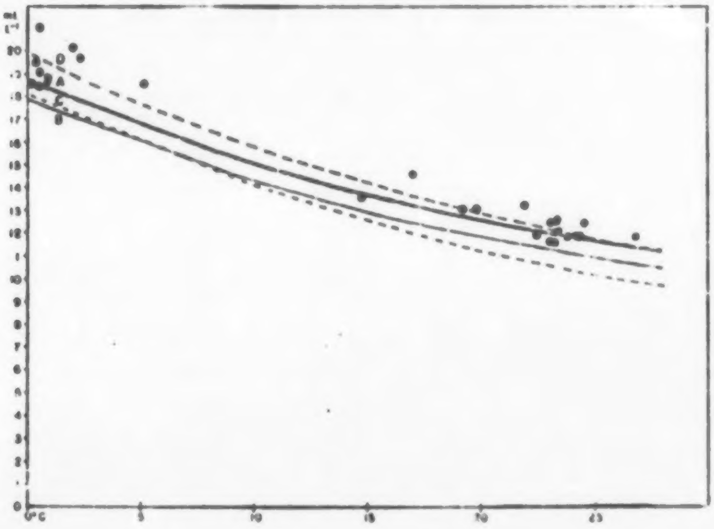
(Data by Carpenter, 1966).

4/1-83

Solubility of Nitrogen

Because of its chemical relative inertness (as a molecular species), relatively little interest attaches to the solubility of nitrogen. Various estimates of the solubility of nitrogen in water as a function of temperature are shown in Figure 1-17

One important aspect of nitrogen solubility is the possibility of supersaturation. Mortality in salmon and trout have been ascribed to gas bubble disease. With an increase in temperature, the originally saturated water becomes supersaturated and the effect of this supersaturation has been discussed for the Chinook salmon "Jacks", by Snyder and Blahm (1971).



The solubility of molecular nitrogen (ml. per liter) in waters at various temperatures. A, solubility computed for dry air at sea level from the determinations of Fox; B, solubility computed for wet air at an elevation of 278 m.; C, curve B corrected for the apparent supersaturation effect in Fox's experiments; D, curve drawn by eye, parallel to C, to fit the determinations made by Birge and Juday on surface waters of Wisconsin Lakes, and presumably a suitable working standard for estimation of saturation in vertical series of analyses by these investigators.

Figure 1-17

Table 1–48

NITROGEN N_2

SOLUBILITY IN WATER

(Winkler, 1891; Bohr and Bock, 1891; Morrison and Billett, 1952)

Results in reasonable agreement with these are given by Braun, 1900; Hufner, 1906–07; Bohr, 1910; Muller, 1912-13; von Hamel, 1915; Cassuto, 1934; Orcutt and Seevers, 1936, 1937; Van Slyke, 1939.

Of the several determinations, Winkler's are generally lowest; above 35° the recent values of Morrison and Billet are considerably higher than the older work.

β = Bunsen absorption coefficient = ml N_2 (at 0°, 760 mm.) dissolved by 1 ml. H_2O when partial pressure N_2 = 760 mm.

$\mathcal{S}$ = "Solubility" = ml N_2 (at 0°, 760 mm) dissolved by 1 ml. H_2O when total pressure (N_2 + H_2O) = 760 mm.

q = gms. N_2 per 100 gms. H_2O when total pressure = 760 mm.

	(M.&B. 1952)	(B.&B. 1891)	(W., 1891)		
t°	β	β	β	$\mathcal{S}$	q
0	—	0.0239	0.0235	0.0233	0.00239
5	—	0.0215	0.0208	0.0206	0.00259
10	—	0.0196	0.0186	0.0183	0.00230
15	0.01745	0.0179	0.0168	0.0165	0.00208
20	0.01599	0.0164	0.0154	0.0151	0.00189
25	0.01485	0.0150	0.0143	0.0139	0.00174
30	0.01377	0.0138	0.0134	0.0128	0.00161
35	0.01283	0.0127	0.0125	0.0118	0.00148
40	0.01215	0.0118	0.0118	0.0110	0.00139
50	0.01125	0.0106	0.0109	0.0096	0.00121
60	0.01085	0.0100	0.0102	0.0082	0.00105
70	0.01058	--	—	--	—
80	—	--	0.0096	0.0051	0.00069
100	—	0.0100	0.0095	0.0000	0.00000

SOLUBILITY OF NITROGEN IN AQUEOUS SALT SOLUTIONS

(Braun, 1900)

	Coefficient of Absorption of N_2 in Barium Chloride Solutions of:				
t°	13.83%	11.92%	6.90%	3.87%	3.33%
5	0.0127	0.0137	0.0160	0.0180	0.0183
10	0.0117	0.0125	0.0147	0.0166	0.0168
15	0.0104	0.0114	0.0132	0.0148	0.0150
20	0.0092	0.0098	0.0118	0.0132	0.0135
25	0.0078	0.0086	0.0104	0.0114	0.0119

	Coefficient of Absorption of N_2 in Sodium Chloride Solutions of:				
t°	11.73%	8.14%	6.4%	2.12%	0.67%
5	0.0102	0.0127	0.0138	0.0179	0.0200
10	0.0093	0.0113	0.0126	0.0164	0.0185
15	0.0081	0.0101	0.0113	0.0147	0.0164
20	0.0066	0.0087	0.0098	0.0131	0.0148
25	0.0047	0.0075	0.0083	0.0113	0.0130

Table I-48

SOLUBILITY OF NITROGEN IN SALT SOLUTIONS

(Morrison and Billet, 1952)

Values of "salting-out" constants $k = \frac{\log So/S}{C}$

So = Solubility in pure H_2O (β)

C = Moles salt per 1000 gms. H_2O.

		k		
t°	So	NaCl	LiCl	KI
12.6	0.01837	0.143	0.125	0.134
30	0.01377	0.121	0.095	0.100
50	0.01125	0.106	0.084	0.086
72	0.1054	0.106	0.092	0.084

SOLUBILITY OF NITROGEN IN SEA WATER

(Fox, 1909a)

Before using the sample of sea water for the solubility determinations it was found necessary to add acid, otherwise the CO_2 could not be boiled out or the precipitation of neutral carbonates prevented. The very small amount of acid was titrated back, using phenolphthaleine as indicator.

The results are in terms of number of cc. of nitrogen (containing argon) absorbed by 1000 cc. of sea water from a free dry atmosphere of 760 mm. pressure.

The calculated formula expressing the solubility is:

$$1000\underline{q} = 18.639 - 0.43041\underline{t} + 0.0074533\underline{t}^2 - 0.0000549\underline{t}^3$$
$$- Cl(0.2172 - 0.007187\underline{t} + 0.0000952\underline{t}^2).$$

Parts Chlorine per 1000	t°=0°	4°	8°	12°	16°	20°	24°	28°
0	18.64	17.02	15.63	14.45	13.45	12.59	11.86	11.23
4	17.74	16.27	14.98	13.88	12.94	12.15	11.46	10.89
8	16.90	15.51	14.32	13.30	12.44	11.70	11.07	10.52
12	16.03	14.75	13.66	12.72	11.93	11.25	10.67	10.16
16	15.18	14	13	12.15	11.73	10.81	10.27	9.80
20	14.31	13.27	12.34	11.57	10.92	10.36	9.87	9.44

A critical examination of the available data upon the Solubility of Nitrogen in pure water and in sea water has been made by Coste, 1917, 1927. It is concluded that "When proper allowances have been made for the effect of argon in the solubility of atmospheric nitrogen, considerable uncertainty exists as to the absorption coefficients of both this mixed gas and pure nitrogen in distilled Water. A similar uncertainty exists in the case of sea water.

B.3. Solubility of Argon and Carbon Monoxide

Solubility data for argon and for carbon monoxide are shown in the Tables included, taken from the solubility listings by Seidell (edited by Linke, 1958).

Table 1-49

ARGON A

THE SOLUBILITY OF ARGON IN WATER

The data of Lannung, 1930 (0°-40°), Morrison and Johnstone, 1954 (10°-80°), Friedman, 1954 (15°, 25°), and Eucken and Hertzberg, 1950 (0°, 20°) are in excellent agreement. The values listed below were read from a smooth curve drawn through the combined data. The average deviation of the original data from the curve is 0.0002.

The results of various earlier workers were not in agreement with each other and were up to 20% higher than these. For earlier work, see: Ramsay, 1895; Estreicher, 1899; Winkler, [illegible], 1906; Von Antropoff, 1910, 1919; Valentiner, 1927, 1930; Akerlof, 1935; [illegible] and Yar[illegible]gh, 1939.

α = Bunsen absorption coefficient. α = ml. of gas (reduced at S.T.P.) dissolved by 1 ml. of solvent when the partial pressure of the gas is 1 atmosphere. See page 2 .

°C	α	°C	α	°C	α
0	0.0528	30	0.0288	60	0.0209
5	.0466	35	.0269	65	.0202
10	.0413	40	.0251	70	.0196
15	.0370	45	.0237	75	.0189
20	.0337	50	.0226	80	.0184
25	.0311	55	.0217		

Table 1-50

CARBON MONOXIDE CO 0

SOLUBILITY IN WATER

The data below are determined by Winkler, 1901. In the following table are some results which do not agree too well with these. See also O'Brien and Parker, 1922. There is no very recent work.

β = Vol. of CO (measured at 0°, 760mm) absorbed by 1 volume of liquid at a partial pressure of CO of 760mm.
β' = Vol. of CO (measured at 0°, 760mm) absorbed by 1 volume of liquid at a total pressure (CO + vapor) of 760mm.
q = Grams of CO dissolved by 100 gms. H_2O at a total pressure of 760mm.

t°	β "Absorp. Coef."	β' "Solubility."	q	t°	β "Absorp. Coef."	β' "Solubility."	q
0	0.03537	0.03516	0.0044	40	0.01775	0.01647	0.0021
5	0.03149	0.03122	0.0039	50	0.01615	0.01420	0.0018
10	0.02816	0.02782	0.0035	60	0.01488	0.01196	0.0015
15	0.02543	0.02501	0.0031	70	0.01440	0.00998	0.0013
20	0.02319	0.02266	0.0028	80	0.01430	0.00762	0.0010
25	0.02142	0.02076	0.0026	90	0.01420	0.00438	0.0006
30	0.01998	0.01915	0.0024	100	0.01410	0.00000	0.0000

SOLUBILITY OF CARBON MONOXIDE IN PHYSIOLOGICAL SOLUTIONS

SOLUBILITY OF PURE CARBON MONOXIDE IN SERUM AND IN PLASMA
(O'Brien and Parker, 1922)

As a check on the determinations the authors also determined the solubility of carbon monoxide in water and obtained results in good agreement with those of Winkler.

t°	Cc. of CO absorbed per 1.0 cc. of Beef serum	Sheep serum	Human serum	Beef plasma
15	0.203	0.0206	....	0.0193
20	0.181	0.0187	0.0160	0.0181
25	0.161	0.0156	0.0183	0.0169
30	0.145	0.0153	0.0158	0.0147
37	0.129	0.0144	0.0142	0.0134

Data for the solubility of CO in ox blood and ox serum at 25° are given by Findlay and Creighton, 1910-11.

Data for the influence of time on the absorption of CO by blood are given by Grehaut (1896). The author passed air containing from one part CO per 1000 to one part CO per 60,000, through 100 cc. portions of blood and found that the maximum absorption, 18.3 cc. CO per 100 cc. of blood (for the 1 : 1000 mixture) occurred in three hours.

Data for the solubility of CO in aqueous hemoglobin solutions are given by Hufner (1895) and Hufner and Kulz (1895).

Treatment of CO_2-Carbonate Systems (with some notes on Calcium sulphate)

In this section, data are shown for the solubility of CO_2 in pure water and, where available, in salt solutions including seawater.

A general treatment of carbonate equilibria has been presented by Garrels and Christ (1965). The discussion is divided by the authors into the following set of typical conditions:

1. Pure calcite and pure water, with negligible gas phase present.
2. Calcium in pure water system open to CO_2 (i.e., in contact with a reservoir such as the atmosphere of fixed partial pressure CO_2).
3. Equilibrium relations with fixed quantity of dissolved carbonate species, but pH arbitrarily fixed (controlled by other reactions).
4. Equilibrium in a system connected to an external reservoir of fixed partial pressure of CO_2 but with pH arbitrarily determined.
5. Equilibrium resulting from addition of $CaCO_3$ to a system originally open to a CO_2 reservoir but closed to that reservoir before addition to $CaCO_3$.

For System I, the temperature dependence can be illustrated. Table 3.2 shows carbonate equilibria (see Garrels and Christ, page 89) at temperatures from 0 to 80° C. Lee has also dealt with the carbonate equilibria; see particularly the survey article (1968). Additional data for carbonate systems were discussed by Kramer (1967). Kramer's data are interesting as they show actual data and calculated values, revealing a complete lack of agreement between theory and experiment. Figures 1-18, 19, 20, 21, 22, 23, and 24 are taken from Kramer's paper.

Table 1-51

Solubility of CO_2 in pure water

Temp., °C.	0.03%	0.033%	0.044%	Temp., °C.	0.03%	0.033%	0.044%
0	1.00	1.10	1.47	16	0.57	0.62	0.84
1	0.96	1.06	1.41	17	0.55	0.60	0.81
2	0.93	1.02	1.36	18	0.54	0.59	0.79
3	0.89	0.99	1.30	19	0.52	0.58	0.76
4	0.86	0.91	1.26	20	0.51	0.56	0.74
5	0.83	0.91	1.22	21	0.49	0.54	0.72
6	0.80	0.88	1.17	22	0.48	0.52	0.70
7	0.78	0.86	1.14	23	0.46	0.51	0.68
8	0.75	0.82	1.10	24	0.45	0.50	0.66
9	0.72	0.79	1.06	25	0.44	0.48	0.64
10	0.70	0.76	1.02	26	0.42	0.46	0.62
11	0.67	0.74	0.98	27	0.41	0.45	0.60
12	0.65	0.72	0.95	28	0.40	0.44	0.59
13	0.63	0.69	0.92	29	0.39	0.43	0.57
14	0.61	0.67	0.89	30	0.38	0.42	0.56
15	0.59	0.55	0.87				

Table 1-52

CARBON DIOXIDE CO_2

SOLUBILITY IN WATER

(1) Bohr (1899); Geffeken (1904); Just (1901); (2) Morgan and Payne, 1930; (3) Markham and Kobe, 1941, 1941a; (4) v. Kiss, Lajtai and Thury, 1937; (5) Showalter and Ferguson, 1936; (6) Gatterer, 1926; (7) Kobe and Williams, 1935; (8) Orcutt and Seevers, 1936, 1937; (9) Kobe and Williams, 1935; (10) Shedlovsky and McInnes, 1935; (11) Curry and Hazelton, 1938; (12) Morrison and Billett, 1952.

The data listed below are those of Bohr (1899), Geffcken (1904) and Just (1901) when unmarked (unmarked values of q and β are not necessarily from the same author). The recent determinations of Morrison and Billett (1952) were plotted and the values of β given in parentheses ( ) were read from the graph. The results of various other authors are in excellent agreement with these. The data of Harned and Davis (1943) are apparently too high by about +.01 in β over the entire 0-50° range. Kunerth's (1922) results 20-34° seem too low (about -.02 in β), as are those of Morgan and Maass (1931) from 0-25° (-.02 to -.1 in β). The data of Buch (1925) at very low partial pressures of CO_2 are erratic. Additional results are given by Bhagwat and Dahr (1929), Appel (1921), Schwab and Berninger (1928), Hantzsch and Vagt (1901) and [of the supersaturation limits] by Metschl (1924).

q = gms. CO_2 dissolved by 100 gms. H_2O at a total pressure of 760mm.

β = ml CO_2 (measured at 0°, 760mm) dissolved in 1 ml. of H_2O when the partial pressure of CO_2 is 760mm.

SOLUBILITY OF CO_2 IN WATER--Cont.

t°	q	β	Other values for β
0	0.335	1.713	1.713 (4) 1.702 (0.2°) (3)
5	.277	1.424	1.419 (6)
10	.231	1.194	1.197 (6)
12.5	...	... (1.075)	1.159 (4)
15	.197	1.019(1.000)	1.022 (5) 1.014 (6)
20	.169	0.878(.865)	0.872 (6)
23	...	...	.802 (7)
24	...	...	.776 (7)
25	.145	.759(.754)	.758 (7) .757 (6)(2) .753 (8) .754(9) .756(3) .750(4) .7553(10) . .752(11)
30	.126	.664(.664)	
35		(.595)	
40	.097	.530(.533)	
45		(.480)	
50	.076	.436(.438)	
55		(.397)	
60		(.365)	
70		(.319)	

Table 1-53

Henry's Law Constants for the Dissolution of CO_2 in Pure Water and Aqueous NaCl Solutions

From H. S. Harned and R. Davis, Jr., *J. Am. Chem. Soc.*, 65, 2030 (1943).

	$-\log C$			
Temp., °C	**Pure Water**	**0.2 *M*, NaCl**	**0.5 *M* NaCl**	**1 *M* NaCl**
0	1.1144	1.1383	1.1738	1.2313
5	1.1938	1.2167	1.2510	1.3065
10	1.2695	1.2920	1.3259	1.3800
15	1.3412	1.3638	1.3970	1.4482
20	1.4063	1.4285	1.4605	1.5110
25	1.4635	1.4842	1.5152	1.5645
30	1.5209	1.5410	1.5712	1.6191

Table 1-54

Carbonate Equilibria

Temperature, °C	pK_1[a]	pK_2[b]	pK_s[c]	pK_{CO_2}[d]
0	6.58	10.62	8.02	1.12 (0.2°)
5	6.52	10.56	8.09	
10	6.47	10.49	8.15	
15	6.42	10.43	8.22	
20	6.38	10.38	8.28	
25	6.35	10.33	8.34	1.47
30	6.33	10.29	8.40	
40	6.30	10.22	8.52	1.64
50	6.29	10.17	8.63	
80	(6.32)	(10.12)	8.98	

$pK_1 = -\log K_{H_2CO_3}$; $pK_2 = -\log K_{HCO_3}$; $pK_s = -\log K_{CaCO_3}$; $pK_{CO_2} = -\log K_{CO_2}$. Values of original authors rounded to two decimal places in present table.

Table 1-55

Solubility of $CaCO_3$ at various temperatures for two important CO_2 pressures

Temp., °C.	0.033%	0.044%	Temp., °C.	0.033%	0.044%
0	96	106	15	67	74
1	95	104	16	65	71
2	93	101	17	63	70
3	90	99	18	62	68
4	88	96	19	60	67
5	86	94	20	59	65
6	84	92	21	57	63
7	82	89	22	56	62
8	79	87	23	55	61
9	77	85	24	54	60
10	75	83	25	54	59
11	73	81	26	52	58
12	71	79	27	51	57
13	69	77	28	50	56
14	68	76	29	49	54

Table 1-56

CO CALCIUM CARBONATE $CaCO_3$

SOLUBILITY IN WATER

Since the reactions $CO_3^{=} \rightleftharpoons HCO_3^-$ and $HCO_3^- \rightleftharpoons CO_2$ aq. are appreciable, the solubility of $CaCO_3$ is dependent on the concentration of CO_2 in solution, and therefore on the partial pressure of CO_2 in the atmosphere above the solution.

Much of the older work has been evaluated by Johnston (1915) and Frear and Johnston (1929) and only data representing some of the more reliable results are reproduced here. For additional (older) data see:

Cossa, 1869; Schloesing, 1872; Caro, 1874; Reid, 1887-88; Irving and Young, 1888; Anderson, 1888-89; Engel, 1888; Lubavin, 1892; Pollacci, 1896; Leather and Sen, 1909; Cavazzi, 1917; Seyler and Lloyd, 1909; Holleman; Treadwell and Renter, 1896; Ramann and Sallinger, 1921.

SOLUBILITY OF CALCIUM CARBONATE IN WATER IN CONTACT WITH ORDINARY AIR
(Wells, 1915)

Joplin, Mo., calcite was used. The solutions were kept in a thermostat and agitated by a current of out-door air filtered through cotton and washed by water. The CO_2 content of the air varied from 3.02 to 3.27 parts per 10,000. The calcium content of the solutions was determined by titrating with 0.02 n $NaHSO_4$, using methyl orange as indicator. The solutions were slightly acid to phenolphthalein, showing that the calcium was present chiefly as bicarbonate.)

SOLUBILITY OF CALCIUM CARBONATE IN WATER IN CONTACT WITH ORDINARY AIR--Cont.

Results in parentheses are by Kendall (1912). In connection with these it is stated by Johnston (1915), that assurance is wanting that the partial pressure of CO_2 was the same at both temperatures and the results are, therefore, not necessarily comparable.

t°	Gms. $CaCO_3$ per Liter	t°	Gms. $CaCO_3$ per Liter
0	0.081	30	0.052
10	0.070	40	0.044
20	0.065	50	0.038 (0.029)
25	0.056 (0.046) 0.052*		

*Frear and Johnston, 1929.

SOLUBILITY OF CALCIUM CARBONATE IN WATER ESSENTIALLY FREE OF CARBON DIOXIDE

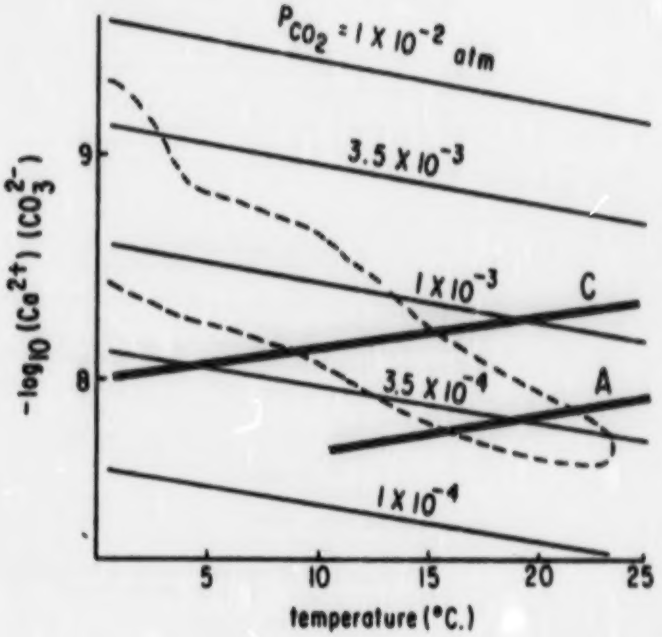
t°	Gms. $CaCO_3$ per liter	Author
15	0.238 (?)	Treadwell and Renter, 1896
17	0.0145	Stumper, 1925
18	0.0128	LeBlanc and Novotny, 1906
25	0.0132	Franquin and Marecaux, 1938
25	0.013	Askew, 1923
"Room t°"	0.013	Wesley, 1944
95	0.024	"
95-100	0.0207	LeBlanc and Novotny, 1906
100	0.0375	Leick, 1932, 1933
182	0.025	Straub, 1932
207	0.014	"
244	0.011	"
316	0.08	"
370	0.39 (200 atm.)	Schloemer, 1952

SOLUBILITY OF CALCIUM CARBONATE IN WATER AT LOW PARTIAL PRESSURES OF CO_2

THE SOLUBILITY OF CALCIUM CARBONATE (CALCITE) IN WATER AT 16° IN CONTACT WITH AIR CONTAINING PARTIAL PRESSURE P OF CO_2
(Calc. from Schloesing, 1872, and Engel, 1888, by Johnston, 1915)

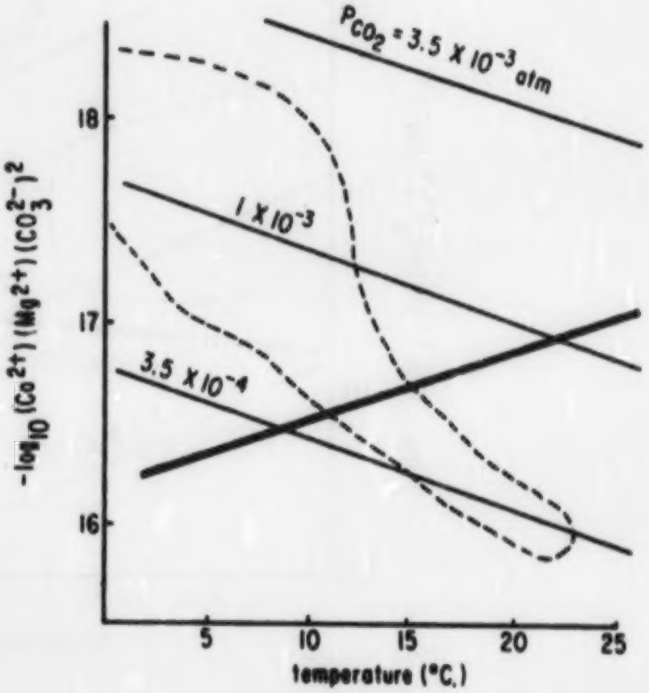
Partial Pressure P of CO_2 in Atmospheres	Total Ca. Mols. per Liter	Total $Ca(HCO_3)_2$ Mols. per Liter
0.000504	0.000746	0.000731
0.000808	0.000850	0.000837
0.00333	0.001372	0.001364
0.01387	0.002231	0.002226
0.02820	0.002965	0.002961
0.05008	0.003600	0.003597
0.1422	0.005330	0.005328
0.2538	0.006634	0.006632
0.4167	0.007825	0.007874
0.5533	0.008855	0.008854
0.7297	0.009772	0.00972

(Cont.)



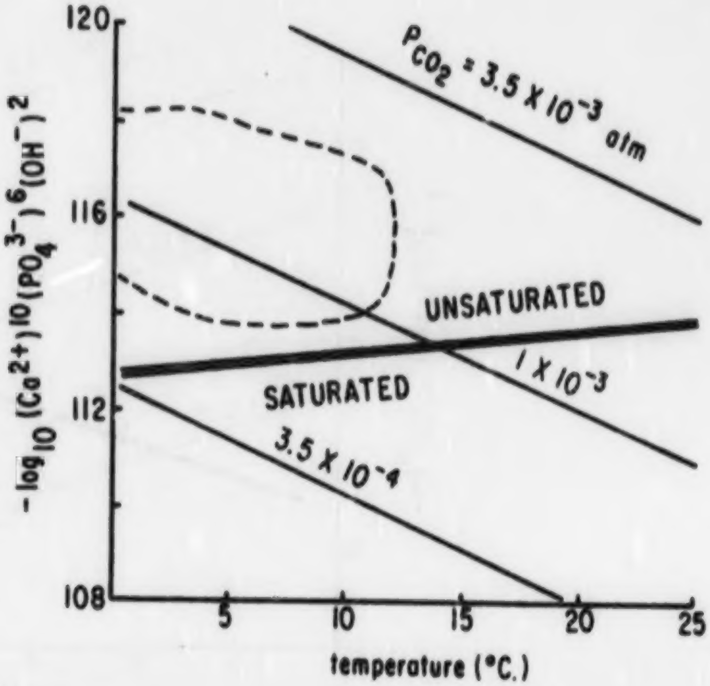
Ion Products for Calcite (c) and Aragonite (a) as functions of Temperature and Partial Pressure of Carbon Dioxide. The actual data from Lake Water Studies Fall Within the Dashed Lines. Double Lines Represent Solubility Constants. (Kramer, in Stumm, 1967, Page 251).

Figure 1-18



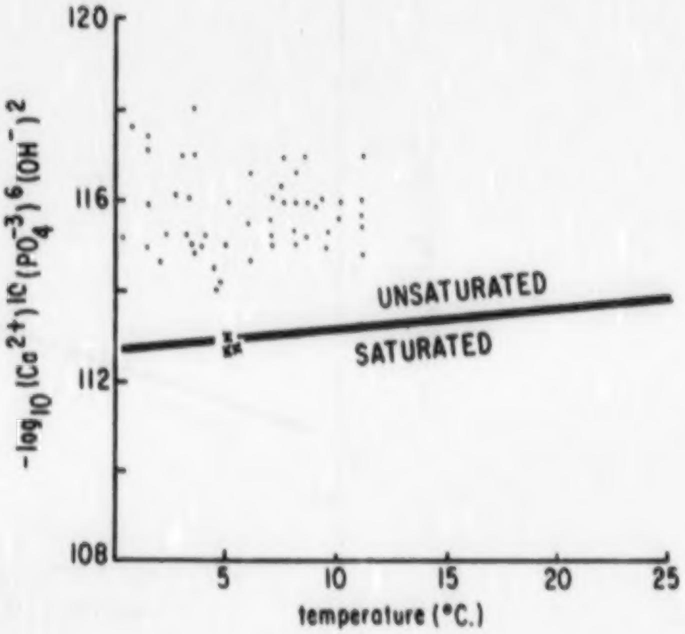
Ion Product for Dolomite as a Function of Temperature and Partial Pressure of CO_2. Double Line Represents Solubility Constant. Areas Indicated by Dashed Line Include Data from Actual Lake Water Analysis (Kramer, See Stumm, 1967, page 252).

Figure 1-19



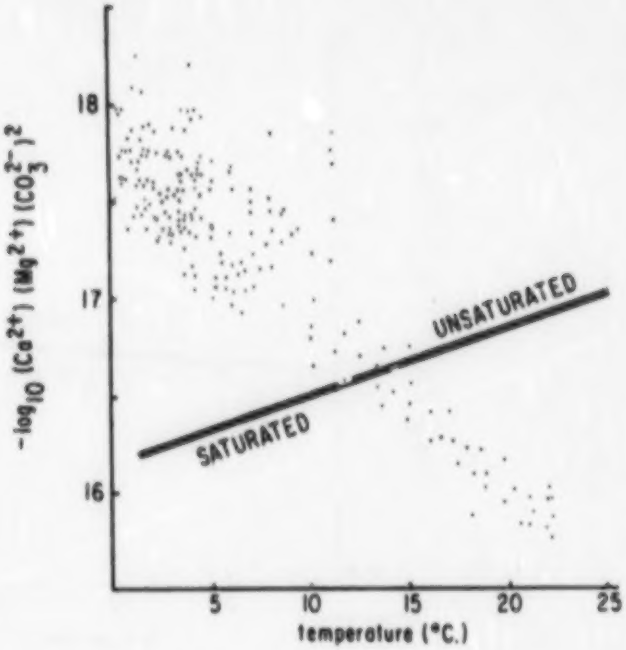
Ion Product for Hydroxyapatite as a Function of Temperature and Pressure. Dashed Line Indicates Actual Values for Observed Data (only during Winter). Double Line Represents Solubility Constant. (Data by Kramer, see Stumm, 1967, page 253).

Figure 1-20



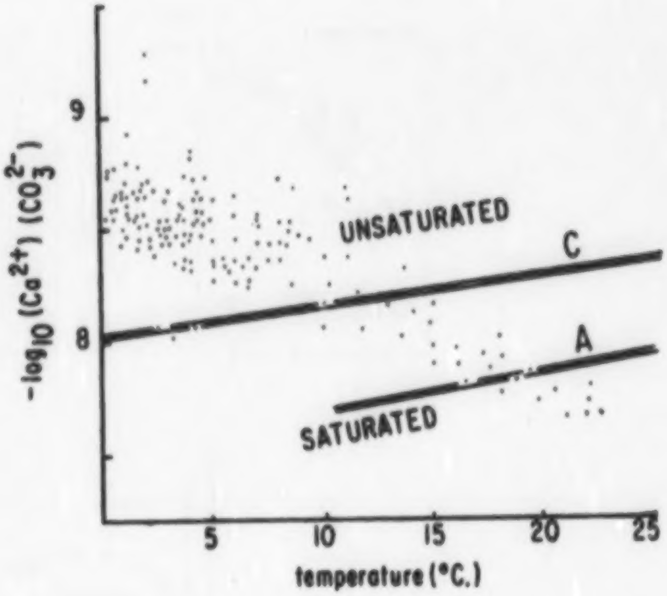
Saturation of Lake Water with Respect to Hydroxyapatite as a function of temperature. Low temperature data available only. (Kramer, in Stumm, 1967, page 249).

Figure 1-21



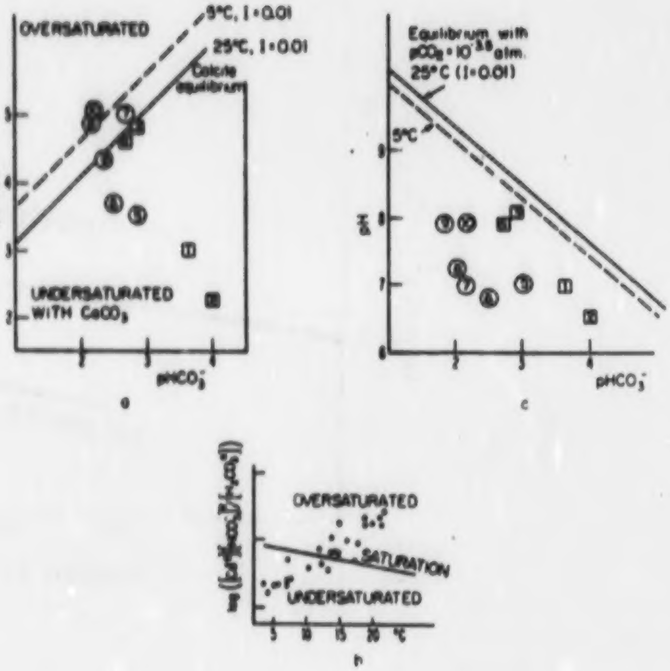
Saturation of Lake Water with Respect to Dolomite as a Function of Temperature. Points Above the Double Line Indicate Unsaturated Conditions; Points Below the Double Line Saturated Conditions. Note the Vastly Different (in fact, opposite) Temperature Coefficient Between Actually Observed and Theoretically Predicted Solubilities. (Kramer, in Stumm, 1967, page 248).

Figure 1-22



Saturation of Lake Water with Respect to Dolomite. Points Above Double Line Correspond to Unsaturated Conditions; Below Dotted Line To Saturated Systems. (Kramer, in Stumm, 1967, Page 248).

Figure 1-23



Actual composition values for carbonates in various lakes and streams. Figure a: actual data from various sources, compared with equilibrium composition for the reaction $CaCO_3(s) + H^+ \rightleftharpoons Ca^{++} + HCO_3^-$. Figure b: water from Lake Zürich; note oversaturation with calcium carbonate at high temperatures (upper layers) and undersaturation at lower temperatures. The deviation from equilibrium is, in part, explainable in terms of photosynthesis (upper layers, with increased pH) and by respiration in deeper layers (decrease in pH). Figure c: oversaturation with respect to CO_2 content of the atmosphere. Actual data from variou locales (streams and lakes). Theoretical lines indicate the equilibrium $CO_2(g) + H_2O \rightleftharpoons H^+ + HCO_3^-$.

Figure I-24

For additional discussions of various aspects of the carbon dioxide carbonate equilibria, see the writings by Sillen (particularly 1961). More recent papers include a study by Pytkowicz (1968), concerned with the carbon dioxide-carbonate equilibria at high pressures. See also the paper by Bischoff (1969) which provides a number of kinetic data (although mostly for temperatures above those of immediate interest in the present connection.

Extensive discussion of the carbon dioxide hydrogen ion concentration and calcium carbonate solubility can also be found in Vol. I of Hutchinson's treatise on limnology (1967).

The effects of temperature on the various equilibrium constants for carbonate equilibria are shown in Table 1-54, from the data by Garrels and Christ (1965, page 89). No reference is made in this review to the changes with pressure as only pressures exceeding about twenty-five atmospheres appear to play a role (corresponding to an effective depth of 250 meters, or roughly 750 feet).

Most of the organic matter in seawater is nitrogenous. The major part of the organic compounds are in the form of peptides, proteins and "heteropolycondensates" (see E. T. Degens in "Organic Matter in Natural Waters", edited by Donald W. Hood, 1970, p. 99). According to Degens, free monomers such as amino acids, fatty acids and sugar amounts to less than 10% of total amount of organic matter. Degens proposes that clathrate-type molecular structures form the heteropolycondensates. As would be expected, Degens concludes that the majority of the organic matter is the result of metabolism of planktons and microorganisms. The contribution to the oceans of land-based sources of organic matter is probably negligible, except in the immediate vicinity of river discharges (estuarine environments).

The difficulties which surround the description of the carbonate equilibria in natural water, brackish water and seawater have been indicated above. Chave (in "Organic Matter in Natural Waters", edited by Donald W. Hood, 1970, p. 373) has contributed to the problem of the calcium carbonate-seawater system, particularly through the suggestion that rates of reactions may be significantly influenced by adsorption of organic material onto the initially-formed carbonates.

Chave summarizes the main problem areas within the carbonate system in the following way:

1) "The supersaturation of most surface and near surface seawaters with respect to calcium carbonate (Wattenberg and Timmerman, 1966, MacIntyre and Platford, 1964).

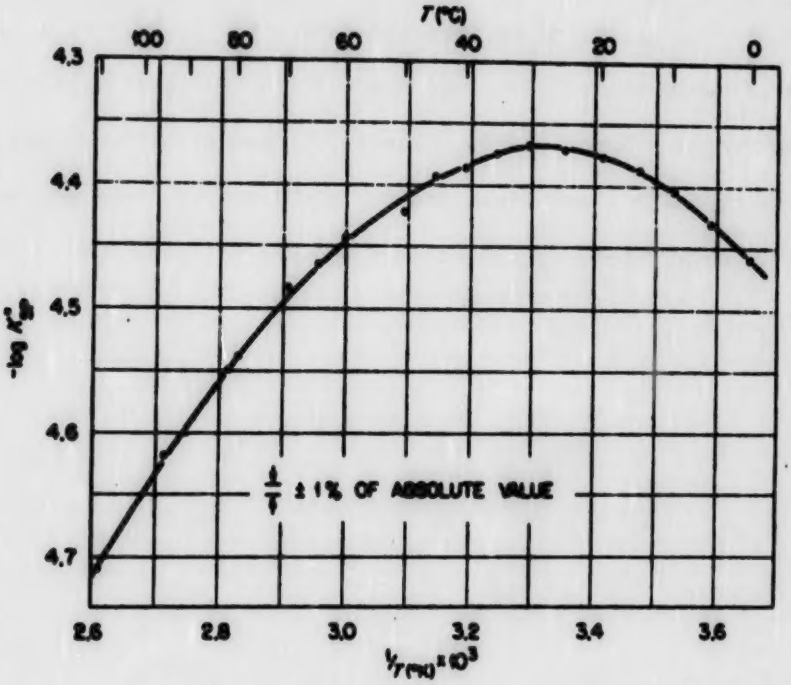
2) "The complex minerality of shelf carbonate sediments (Land, 1961, Figure 1).

3) The occurrence of $CaCO_3$ in pelagic sediments from all depths of the ocean (Bramlette, 1961; Smith, _et al_., 1968)".

Chave points out that these features suggest the lack of equilibrium in the carbonate-seawater. Thus, solution of calcium carbonate should not remain supersaturated indefinitely (i.e., exhibit the properties of a diuternal supension; see further discussion of colloidal aspects in Section IV). Chave also points out that a complex of calcium carbonate mineral basis cannot be in equilibrium with a single aqueous phase. Finally, the deep ocean waters are undersaturated with respect to calcium carbonate, and hence, carbonates should be absent in deep pelagic sediments. An important conclusion by Chave and Chave and co-workers is that independend work has shown that any seawater sample will equilibrate with (at least) the surface of any marine carbonate mineral within a relatively short time (of the order of an hour). Hence, some aspects other than simply a slow ionic reaction between the inorganics of the system must be involved. This missing aspects appears from the studies by Chave and Chave and co-workers to be the interaction between dissolved organic molecules and the carbonated minerals. The reader is referred to the detailed studies by Chave and co-workers (see Chave, loco cit., 1970). The important aspect to stress at this point is that it apparently is not sufficient to have available temperature coefficients for solubility products, dissociation constants, or even individual rate reactions of carbonate systems in well defined systems. In addition, it is necessary to know in detail the nature of the organic species present in the natural waters, and specifically the degree and rate of adsorption (and co-precipitation) of organic material on freshly formed carbonate particles. Such data are obviously completely lacking at present. Furthermore, an enormous complexity must be anticipated in view of the literally infinite number of possible combinations of concentrations and types of organic solute species. Finally, and this may be particularly significant, although difficult to demonstrate, the rates and the types of reactions may be determined to a large extent by the hydration structures of both the adsorbates and adsorbents.

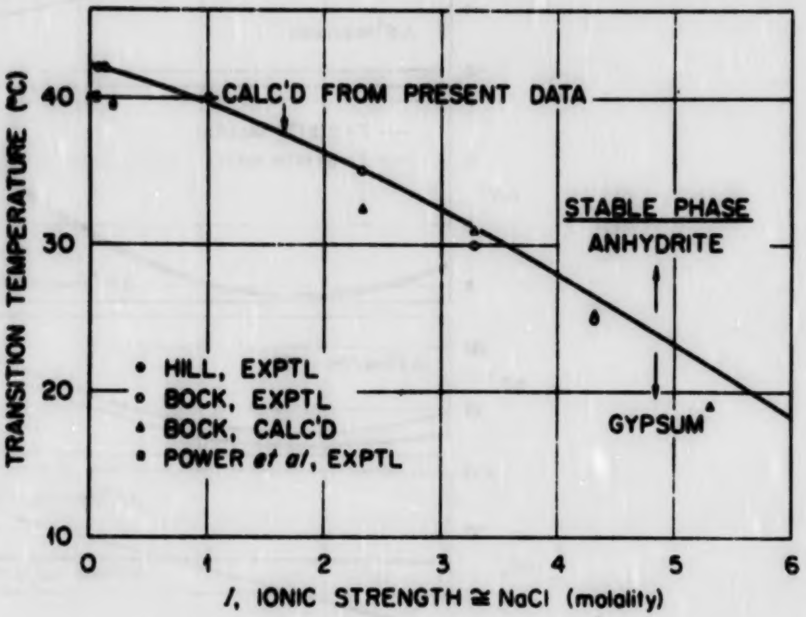
Calcium-Sulfate Solubility Relationships

The temperature dependence of the solubility and stabilities of various calcium sulfates have been treated extensively by Marshall and co-workers, including table of the solubility product as a function of temperature plus graphs of various parameters for solubility as a function of temperature. See also the note in "Properties of Solutions" [OSW, R&D Progress Report, #685, page 117]. See also the volume on solubility by Seidell and Linke and the monograph by Stumm and Morgan (loco cit., page 416-417); and Garrels and Christ (page 106).



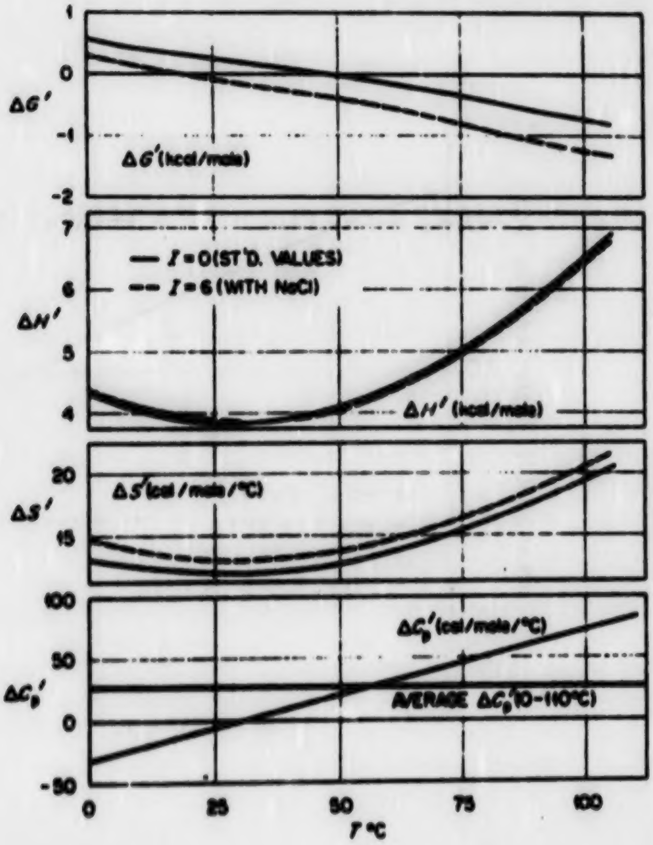
Negative values of logarithmic solubility product constant for $CaSO_4$, $2H_2O$ at zero ionic strength, over a wide range of temperatures. (Marshall and Slusher, 1966).

Figure I-25



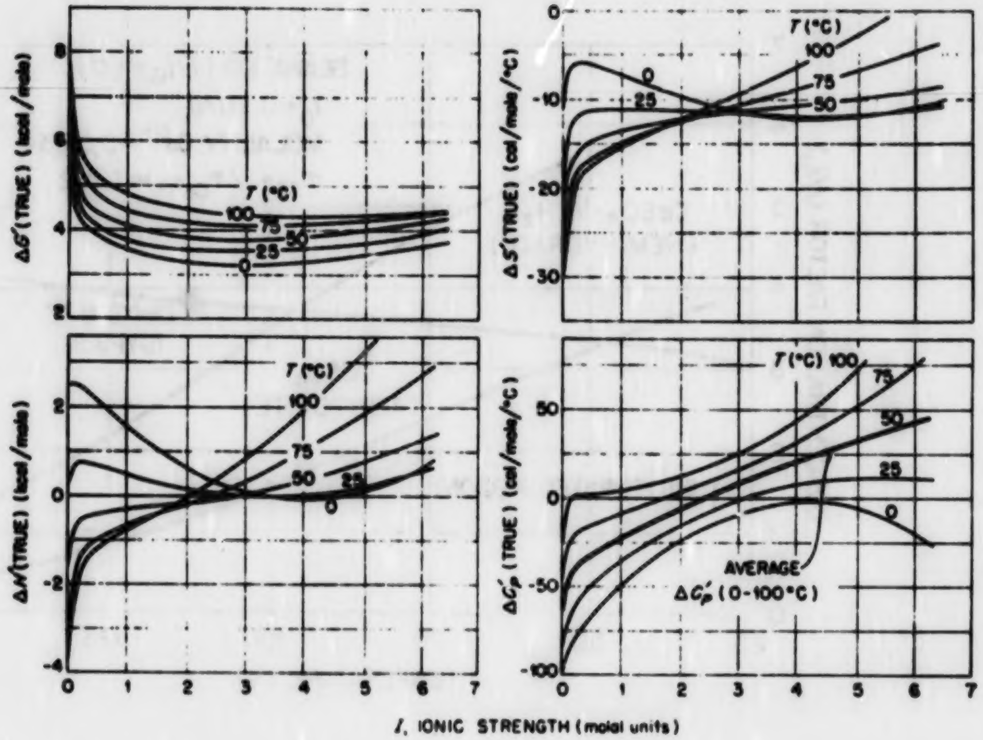
Transition temperatures for gypsum-anhydrite as a function of ionic strength (approximately equal to sodium chloride molality). (Marshall and Slusher, 1966).

Figure I-26



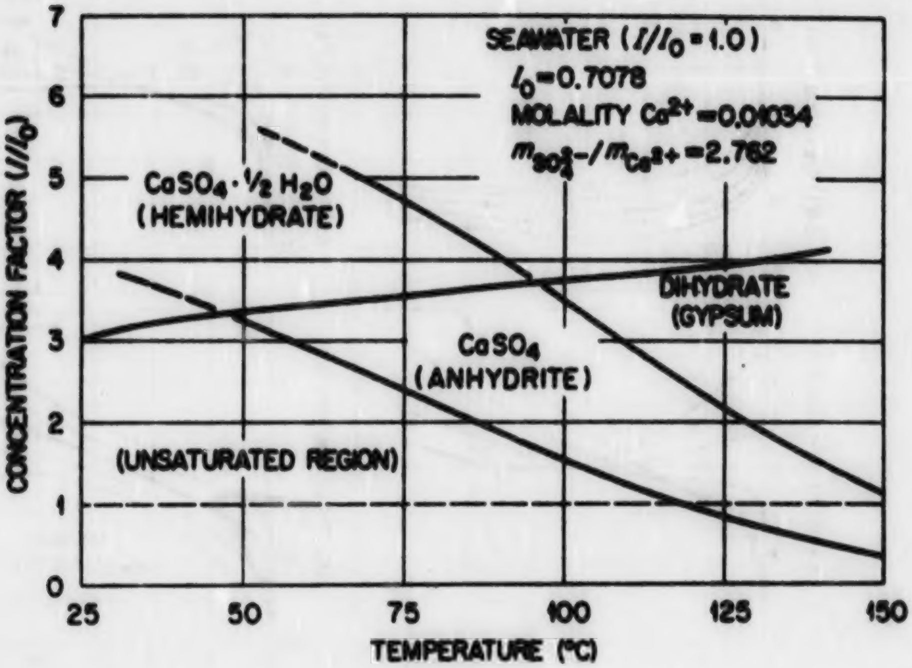
Some thermodynamic values for the reaction $CaSO_4 \cdot 2H_2O^{(s)} \rightleftharpoons CaSO_4^{(s)} + 2H_2O^{(liq)}$. (Marshall and Slusher, 1966).

Figure I-27



Generalized thermodynamic quantities for the solubility of gypsum ($CaSO_4 \cdot 2H_2O$) in sodium chloride-water solution. 0 to 6 molar from 0 to 100° C. (Marshall and Slusher, 1966).

Figure 1-28



Temperature-concentration limits for precipitation of calcium sulfate and its hydrates in seawater. (Marshall, 1971).

Figure 1-29

CO MAGNESIUM CARBONATE $MgCO_3$
HCO MAGNESIUM BICARBONATE $Mg(HCO_3)_2$

SOLUBILITY IN "CO_2-FREE" WATER

At 15°

Extrapolation of the data of Treadwell and Reuter, 1898 shows that at 0 partial pressure of CO_2 and at 15° and mean barometric pressure, one liter of saturated aqueous solution contains 0.641 gm. of $MgCO_3$ plus 1.954 gms. $Mg(HCO_3)_2$.

At 100°
(Leick, 1932, 1933)

The determinations showed that 0.030 gm. MgO = 0.063 gm. $MgCO_3$ per liter was dissolved at 100°. It was found that the solubility is increased by NH_4Cl and Na_2SO_4. NaOH and Na_2CO_3 do not reduce the solubility of $MgCO_3$ as much as they do that of $CaCO_3$. Results for the simultaneous solubility of $MgCO_3$ and $CaCO_3$ in water at 100° show that with increasing time of boiling, from 1-1/2 to 48 hours, the dissolved CaO increased about 5 times while the dissolved MgO decreases about 10 times. The results are of interest in connection with the purification of boiler waters.

RESULTS IN WATER WITH UP TO 1 ATM. PARTIAL PRESSURE OF CO_2

At 15°

Considerable data are given by Treadwell and Reuter, 1898, giving total Mg^{++}, HCO_3^-, and $CO_3^=$, but it is pointed out by Johnston (1915) that although Treadwell and Reuter made very painstaking analyses, their mode of working did not secure equilibrium conditions, a fact which is borne out by the lack of constancy of the calculated solubility-product constant.

At 18°
(Johnston, 1915)

It is shown that if the CO_2 pressure is kept constant at P and the water evaporated off so slowly at 18° that equilibrium conditions are continuously maintained, the following amounts of $Mg(OH)_2$ or of $MgCO_3 \cdot 3H_2O$ will be obtained.

Partial Pressure P of CO_2 in Atms.	Total Mg Mols./l	Gms. per Liter	
0	0.00015	0.0087	$Mg(OH)_2$
0.00020	0.01934	1.13	"
0.00025	0.02218	1.29	"
0.00030	0.02486	1.45	"
0.00035	0.02742	1.60	"
0.00040	0.02868	3.97	$MgCO_3 \cdot 3H_2O$
0.00045	0.02924	4.05	"
0.00050	0.02976	4.12	"

CO
HCO

At 20°
(Wells, 1915)

Mixture	Milligrams per Liter of Sat. Solution Mg	 Free CO_2	 CO_2 as Bicarbonate
Natural Magnesite in Distilled H_2O	0.018	trace	0.069
" in Aq. NaCl (27.2 g. per l)	0.028	trace	0.086
$MgCO_3 \cdot 3H_2O$ (equilibrium from bicarbonate end)	0.038	0.28*	0.83
$MgCO_3 \cdot 3H_2O$ (" " undersaturation")	0.034	0.32*	0.54

* = CO_2 as carbonate

Table 1-57

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Table I-57 Continued

At 25°
(Kline, 1929)

The saturated solutions were prepared by bubbling mixtures of carbon dioxide and air in constant proportions through conductivity water in contact with finely divided solid for periods of three to five days.

Partial Pressure of CO_2 in Atmospheres	Millimols per 1000 gms. H_2O			Partial Pressure of CO_2 in Atmospheres	Millimols per 1000 gms. H_2O		
	$[Mg^{++}]$	$[HCO_3^-]$	$[CO_3^{--}]$		$[Mg^{++}]$	$[HCO_3^-]$	$[CO_3^{--}]$
0.000107	0.00433	0.00488	0.00189	0.000810	0.01437	0.01720	0.00182
0.000113	0.00445	0.00501	0.00195	0.000820	0.01512	0.01872	0.00176
0.000170	0.00577	0.00745	0.00205	0.000845	0.01566	0.01950	0.00172
0.000177	0.00593	0.00763	0.00212	0.000887	0.01593	0.02036	[illegible]
0.000197	0.00658	0.00795	0.00261	0.000930	0.01624	0.02119	0.00165
0.000210	0.00708	0.00806	0.00305	0.00160	0.01859	0.02698	0.00150
0.000233	0.00780	0.00837	0.00361	0.00334	0.02210	0.03548	0.00136
0.000251	0.00807	0.00855	0.00380	0.00690	0.02507	0.04468	0.00123
0.000310	0.01013	0.01184	0.00421	0.0150	0.03127	0.06022	0.00116
0.000376	0.01296	0.01404	0.00594	0.0432	0.04601	0.08958	0.00102
0.000380	0.01355	0.01432	0.00639	0.1116	0.06266	0.1236	0.00085
				0.9684	0.2135	0.4269	—

The activity product constant of magnesium carbonate at 25° is taken as 1 x 10^{-5} and that of magnesium hydroxide similarly as 5 x 10^{-12}.

Table I-58

SOLUBILITY PRODUCTS OF VARIOUS HYDRATES
(Langmuir and Torborg-Jensen, 1949)

$MgCO_3 \cdot 3H_2O$	Ksp = 8.9 x 10^{-6}
$MgCO_3 \cdot 2H_2O$	Ksp = 2.3 x 10^{-5}
$MgCO_3 \cdot H_2O$	Ksp = 2.7 x 10^{-5}

AT OTHER TEMPERATURES

EQUILIBRIUM IN THE SYSTEM MAGNESIUM OXIDE, CARBON DIOXIDE AND WATER
(Takahashi, 1927)

CO
HCO

t°	d. of sat. sol.	Gms. per 100 gms. sat. sol.		Solid Phase
		CO_2	MgO	
-1.80	1.0411	3.410	1.526	$MgCO_3 \cdot 5H_2O$
0	1.0407	3.219	1.496	"
+5	1.0395	2.942	1.423	"
10	1.0383	2.962	1.363	"
15	1.0373	2.744	1.312	"
20	1.0363	2.606	1.256	"
5	1.0407	3.232	1.530	$MgCO_3 \cdot 3H_2O$
10	1.0360	2.736	1.314	"
15	1.0320	2.270	1.143	"
20	1.0287	2.109	0.9858	"
25	1.0250	1.839	0.8654	"
30	1.0210	1.572	0.7634	"
35	1.0170	1.381	0.6780	"
40	1.0135	1.206	0.6017	"
45	1.0097	1.044	0.5323	"
50	1.0050	0.922	0.4718	"
55	1.0008	0.833	0.4083	"
60	0.9980	0.746	0.3648	"

Results are also given for the solubility of $5MgO \cdot 4CO_2 \cdot 7H_2O$ in Water saturated with CO_2 at one atmosphere pressure.

Determinations of the equilibrium in the system $MgCO_3 + CO_2 + H_2O$ made by passing CO_2 at atmospheric pressure through mixtures of H_2O + MgO and $H_2O + MgCO_3$ at temperatures from 0° to 40°, are given by Terada, 1928. There is, however, some uncertainty in regard to the exact terms in which the results are expressed.

Data for the system magnesium carbonate-carbonic acid-water at 20°, 25°, 30°, 34° and 35° are given by Leather and Sen (1914). In connection with these results, it is pointed out by Johnston (1915), that it is questionable whether equilibrium was really obtained and furthermore, the accuracy of the analytical results cannot be trusted since the ratio of total amount of CO_2 in solution, to the magnesia is very irregular. The results when plotted directly show great inconsistencies.

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Solubility Tables

The most extensive listings of solubilities have been presented in the treatise by Seidell (new edition, edited by Linke, 1958). From these tables are taken some illustrative examples of available solubility data (various lead compounds, etc.).

Solubility of Silver Chloride in Water

t°	Gms. AgCl per liter	t°	Gms. AgCl per liter
0	0.00070	40	0.0036
5	0.00085	45	0.0043
10	0.00105	50	0.0054
15	0.00125	100	
20	0.00155	220	
25	0.00193	250	
30	0.0024	269	
35	0.0029	289	

Table 1-59

Table 1-60

Cl LEAD CHLORIDE $PbCl_2$

SOLUBILITY IN WATER

(1) Demassieux, 1923; (2) Flöttmann, 1928; (3) Deacon, 1927; (4) Weber, 1929; (5) Burvage, 1926; (6) Herz and Hellebrandt, 1923; (7) Sowerby, 1927; (8) Lichty, 1903; (9) Carmody, 1929; (10) Lewin, Vance and Nelson, 1953; (11) Benrath, Gjedebo, Schiffers and Wunderlich, 1937; (12) Coulden and Hill, 1945.

For more recent data on the solubility between 100 - 370° see Malinin, 1957.

Solid phase is anhydrous

t°	Gms. $PbCl_2$ 100 gms. sat. sol.		t°	Gms. $PbCl_2$ per 100 gms. sat. sol.		t°	Gms. $PbCl_2$ per 100 gms. sat. sol.	
0	0.668	(8)	15	0.866	(12)	25	1.076	(2)[c]
15	0.922	(8)	20	0.971	(2)[b]		1.075	(3)
	0.85	(1)		0.968	(12)		1.059	(10)
	0.876	(2)[a]	25	1.073	(8)(9)		1.028	(4)

(Cont.)

[a]d. = 1.0071 [b]d. = 1.0070 [c]d. = 1.0069

SOLUBILITY IN WATER--Cont.

(1) Demassieux, 1923; (2) Flöttmann, 1928; (3) Deacon, 1927; (4) Weber, 1929; (5) Burvage, 1926; (6) Herz and Hellebrandt, 1923; (7) Sowerby, 1927; (8) Lichty, 1903; (9) Carmody, 1929; (10) Lewin, Vance and Nelson, 1953; (11) Benrath, Gjedebo, Schiffers and Wunderlich, 1937; (12) Goulden and Hill, 1945.

Solid phase is anhydrous

t°	Gms. $PbCl_2$ per 100 gms. sat. sol.		t°	Gms. $PbCl_2$ per 100 gms. sat. sol.		t°	Gms. $PbCl_2$ per 100 gms. sat. sol.	
20	1.083	(5)(6)	65	2.032	(8)	230	11.3	(11)
	1.075	(12)	80	2.555	(8)	257	14.3	(11)
30	1.17	(8)	95	3.068	(8)	276	16.7	(11)
	1.179	(12)	100	3.234	(8)	287	18.4	(11)
35	1.307	(8)		3.10	(1)	345	24 - 76*	(11)
	1.298	(12)	141	4.74	(11)	351	81.2	(11)
45	1.543	(8)	160	5.67	(11)	362	87.8	(11)
50	1.75	(1)	187	7.39	(11)	407	84.4	(11)
55	1.709	(8)	195	8.47	(11)			

*Two liquid layers are formed and there is present salt solution, melt and vapor.

SOLUBILITY OF LEAD CHLORIDE IN WATER - DEUTERIUM OXIDE MIXTURES AT 25°

(Noonan, 1948)

% D_2O	Moles $PbCl_2$ per 100 moles Solvent
91.6	0.0471
100.0	.0449

Table I-61

LEAD SULFATE $PbSO_4$

SOLUBILITY IN WATER

(Average curve from gravimetric results of Dibbits (1874), Beck and Stegmüller (1910) and Pleissner (1907) and conductivity results of Böttger (1903) and Kohlrausch (1904-05).

t°	Gms. $PbSO_4$ per Liter	t°	Gms. $PbSO_4$ per Liter
0	0.028	20	0.041
5	0.031	25	0.045
10	0.035	30	0.049
15	0.038	35	0.052
18	0.040	40	0.056

Later determinations of the solubility of lead sulfate in water by Crockford and Brawleys, 1934; Purdum and Rutherford, 1933; Kolthoff and Rosenblum, 1933; and Huybrechts and de Langeron, 1930, gave an average curve from which the following values were taken.

t°	Gms. $PbSO_4$ per Liter	t°	Gms. $PbSO_4$ per liter
0	0.0330	25	0.0452
5	0.0354	30	0.0476
10	0.0380	35	0.0500
15	0.0403	40	0.0526
20	0.0427	50	0.0574

Koizumi, 1950 reports that the effect of dissolved CO_2 on the solubility of $PbSO_4$ is negligible.

Table 1-62

MANGANESE CARBONATE $MnCO_3$

SOLUBILITY OF MANGANESE CARBONATE IN WATER
(Smirov, 1938)

(The total pressure of CO_2 + H_2O was one atmosphere)

Partial Pressure CO_2 in atm.	Gms. Mn per 100 gms. Sat. Sol.				
	5°	15°	40°	50°	80°
0.0005	0.0011	0.0009	0.0003	0.0002	0.0001
0.005	.0026	.0022	.0008	.0006	.0002
0.05	.0061	.0052	.0019	.0014	.0005
0.10	.0078	.0068	.0025	.0018	.0007
1.0	--	.04 (16°)*	--	--	--
56	--	.080 (16°)*	--	--	--

Table 1-63

STRONTIUM SULFATE $SrSO_4$

SOLUBILITY OF PRECIPITATED STRONTIUM SULFATE AND OF CALCINED "CELESTINA" (96.67% $SrSO_4$) IN WATER
(Gallo, 1935)

t°	Gms. $SrSO_4$ per 100 cc sat. sol.	
	Solid Phase Pptd. $SrSO_4$	Solid Phase "Celestina"
5	0.0121	0.0119
10	0.0129	0.0123
20	0.0132	0.0132
30	0.0138	0.0136
40	0.0141	0.0136
50	0.0135	0.0128
60	0.0131	0.0125
70	0.0123	0.0119
80	0.0116	0.0111
90	0.0115	0.0107
95	0.0113	0.0108

Results of Kohlrausch, 1908

2.85°	0.01133 gms. per 100 cc H_2O
17.4	0.01143 gms. per 100 cc H_2O
32.3	0.01143 gms. per 100 cc H_2O

In general, temperature changes result in measureable and sometimes significant changes in ion concentration due to dissolution or precipitation of relatively insoluble compounds. Examples of temperature-dependent solubility data are shown in a number of tables. In this review, attention is called, in passing, to these solubility data as indicative of the orders of magnitude which one can expect. However, the reader is warned against drawing inferences about the direct applicability of these data to natural water systems. As will be discussed briefly in Section IV, the actual precipitation or degassing from a slightly supersaturated solution (resulting, for instance, from a lowering of temperature, or say, loss of CO_2) is often slow, and frequently highly dependent on the concentration and nature of heterogeneous nuclei for gas bubble formation or for the initial condensation of the insoluble precipitate. Conversely, the process of dissolution is time-dependent, and an immediate increase in temperature does obviously not immediately result in a new level of concentration of all species to an equilibrium value. Kinetic effects are important and unfortunately these are frequently poorly understood; furthermore, they are highly dependent on specific details on the nature of water and solutes adjacent to the dissolving or precipitating particle (stagnant layers, diffusion boundaries, adsorbed ions or coprecipitated, etc.).

For some comments on complex ions in brine and particularly the difficulties in predicting solubilities of minerals in more concentrated brines, see the discussions by Garrels and Christ (p. 108). These authors particularly note, regarding solubility problems, that theoretical predictions are nearly impossible at the present time. The reason is the unknown contributions to solubility from species for which dissociation constants are not known. Furthermore, the authors also point out that a very large number of simultaneous equations would have to be solved and that the problem, therefore, exceeds what is practical. Accumulation of errors from various uncertainties is presumably known dissociation constants might add up sufficiently to obviate any accuracy in prediction of the activity coefficients. This problem is of some interest in connection with the thermal changes in a natural water system where sediments in contact with the waters may or may not be affected by solubility changes.

Regarding the complex problem of the solubility of silicates, see Garrels and Christ (1965) and also Stumm and Morgan (1970 , loco cit., p. 409).

PART I

SECTION IV: SURFACE AND COLLOID CHEMICAL ASPECTS

IV. SURFACE AND COLLOID CHEMICAL ASPECTS

A. Introduction

The stability of a closed system - any chemical system, and in this case specifically natural waters - is determined by the free energy, ΔF, and for this reason, much interest attaches to the question of possible compensation between enthalpy and entropy; the compensation problem is treated in Section 2-IIIB. For most simple inorganic solutes in water, the thermodynamic properties are fairly well known, permitting various types of calculations of stabilities. However, for more "complicated" solutes, particularly polypeptides, and enzymes, ΔF may be numerically very small, and rather minute "environmental" changes (that is, in the chemical or physical nature of the aqueous system), may affect stability severely. We are presently a long way from a rational - let alone complete - description of natural waters in such terms.

While many unknowns still remain to be determined quantitatively in free energy relationships, the principles of thermodynamics must apply. However, the rate with which the various equilibria may be reached are subject to far greater uncertainty. The problem of colloidal stability continues to be a field of active research. This Section presents a brief outline, in qualitative terms, of the problem of colloid stability. The kinetics of approach to equilibrium in colloidal systems is exceedingly complex. Even in its simplest form, in terms of "classical approaches", the problom is difficult. To these difficulties, the present author feels must be added the very poorly understood (and still incompletely documented) roles of vicinal water structures.

Tables I-64 and I-65 outline in an exceedingly schematic fashion, the standard approach to problems such as colloidal stability, based primarily on theories for the electrical double-layer. Extensive treatments can be found in standard references such as Kruyt (1949, 1952), Adamson (1960), Sheludko (1966), or Davies and Rideal (1963).

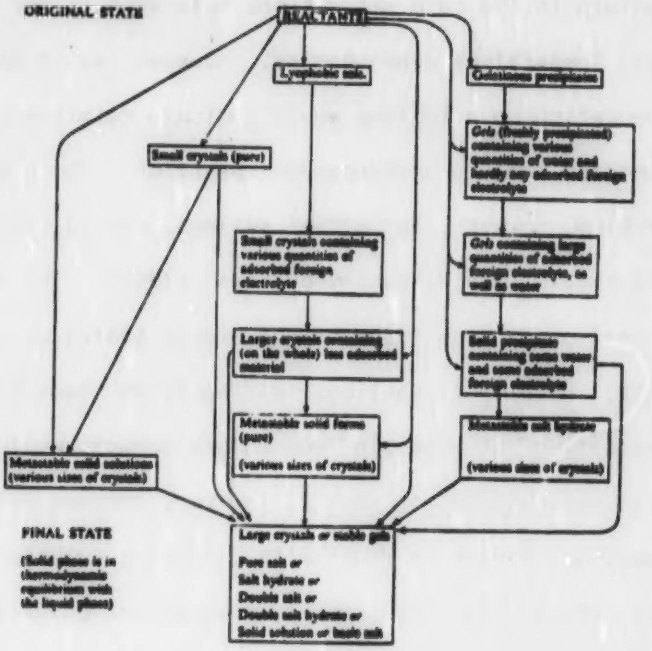
In nearly all of the commonly employed descriptions of surface and colloid phenomena, the assumption is made that "water is water is water"; in other words, that a colloidal system can be considered a heterogeneous mixture of some "extraneous material" in a matrix of water, the latter retaining its bulk structure and properties. Some evidence is accumulating which indicates that water near interfaces is not bulk-like but is indeed differently structured. Furthermore, and perhaps more significantly, the distances over which these different structures extend may be considerable. In this context, "considerable" means large on a molecular scale, say 100 to 1,000 molecular diameters. This is significant in connection with the subject at hand, namely the suitability of natural waters to support life. First of all, the extensive hydration phenomena which may accompany the presence of colloidal material in actual waters may play an important role in determining the overall properties. However, perhaps far more significant is the fact that if indeed water structure is affected over distances of 1,000 molecular diameters (i.e., 0.3 microns), structural effects apparently occur over distances which are of the same order of magnitude as intracellular dimensions. For this reason, it is important first to review briefly some of the available evidence which suggests structuring of water near interfaces. Secondly, attention is directed toward biological systems. Here it is necessary and important to realize that the structural effects observed in cellular systems are found as well in physico-chemically well described, completely non-living systems.

While temperature effects on thermodynamic equilibrium properties may be predicted with some degree of certainty - and generally with predictably small net changes — the behavior of kinetic phenomena is notably different. Rates of reactions are often significantly affected by temperature. However, to the degree of approximation used in this review, the temperature effects on rates are essentially predictable from simple analysis. No sudden or unexpected large changes in the rates of reactions are to be expected for "standard simple processes" such as rate of dissociation of H_2CO_3 - or rate of complexing of magnesium ions. However, unfortunately, these reactions - of the type which occur wholely in bulk - are fairly few and in many respects unimportant for the natural waters. Of far greater importance are those reactions which take place at interfaces. Indeed, these are, by far, the more abundant and include such important properties as rates of transfer of gases at the air/water interface; rates of dissolution or precipitation; rates of reactions involving colloidal suspended matter and the constituents of the natural waters, etc. For reactions involving interfacial aspects, the simple predictions made on the basis of homogeneous bulk reaction rates are often totally incomplete and, in fact, erroneous. The reason for these difficulties is due to the complexities of interfacial phenomena, particularly in aqueous systems where various types of hydration of interfaces is not only still poorly understood, but obviously exceedingly complex.

As will be apparent from the preceding discussion, the bulk properties of water (both physical and chemical properties) may be expected to change in relatively predictable, "smooth" fashion with temperature at least over the temperature interval of practical interest (here chosen to be approximately 0 to 45°C). However, large surface-to-volume ratio systems (such as colloidal suspensions) may be expected to show abrupt and unexpected changes at a number of critical temperatures. The ranges of temperature which have been previously described, particularly by the present author (1973, 1971) are 14 to 16°; 29 to 32°; 44 to 46°; and 59 to 62°. Note that the changes are abrupt, but not of the type of abruptness observed at the freezing or boiling point . This corresponds to the contention made earlier that the anomalies are reflections of higher-order phase transitions (not first order phase transitions). In order to observe higher-order phase transitions, it is necessary to have some structured elements and these are most likely stabilized water structures at the water/solid interface. The higher-order phase transition, in a sense, resembles "smeared out" melting processes of different predominant structures, or rather the transition from one type of structure to another type of structure (with greater stability in a different temperature interval).

Lyophobic suspensions undoubtedly represent an important class of suspended colloidal matter in natural waters. Such colloidal solutions are, in principle, unstable. Essentially, they are unstable because the large surface-to-volume ratio imples a very high surface-free energy content. Lyophobic suspensions have been studied extensively under laboratory conditions but very little information is currently available regarding the stability or even the nature of lyophobic colloids in natural waters. However, it seems reasonable that colloidal organic material does occur in natural waters as the result of biological activity, and it is also likely that these colloids in turn, play important roles in selected systems. Thus, as mentioned in Section IIICl adsorption of such organic colloids as denatured proteins may seriously affect nucleation and precipitation rates of carbonates. Again, one is dealing with an interfacial system for which it is to be expected that hydration structures play a role over and above that recognized in the traditional treatment of colloidal stability.

Lewin (1960) has indicated some possible steps in the creation of a simple precipitate or stable gel from the reactions via various types of precipitates. These include (in order of increasing complexity and practical and theoretical "messiness" metastable solids [crystallites], stable but small crystals, lyophobic sols and gels and gelatinous precipitates of various types (see Figure I-26). The question of the role of water structure in the stability and properties of gels remains unresolved at this time.


ORIGINAL STATE
REACTANTS
Lyophobic sols
Gelatinous precipitates
Small crystals (pure)
Gels (freshly precipitated) containing various quantities of water and hardly any adsorbed foreign electrolyte
Small crystals containing various quantities of adsorbed foreign electrolyte
Gels containing large quantities of adsorbed foreign electrolyte, as well as water
Larger crystals containing (on the whole) less adsorbed material
Solid precipitate containing some water and some adsorbed foreign electrolyte
Metastable solid forms (pure) (various sizes of crystals)
Metastable salt hydrate (various sizes of crystals)
Metastable solid solutions (various sizes of crystals)
FINAL STATE
(Solid phase is in thermodynamic equilibrium with the liquid phase)
Large crystals or stable gels
Pure salt or
Salt hydrate or
Double salt or
Double salt hydrate or
Solid solution or basic salt

Non-stable Intermediary States Which may Form in a Typical Precipitation Reaction (Lewin, 1960).

Figure I-26

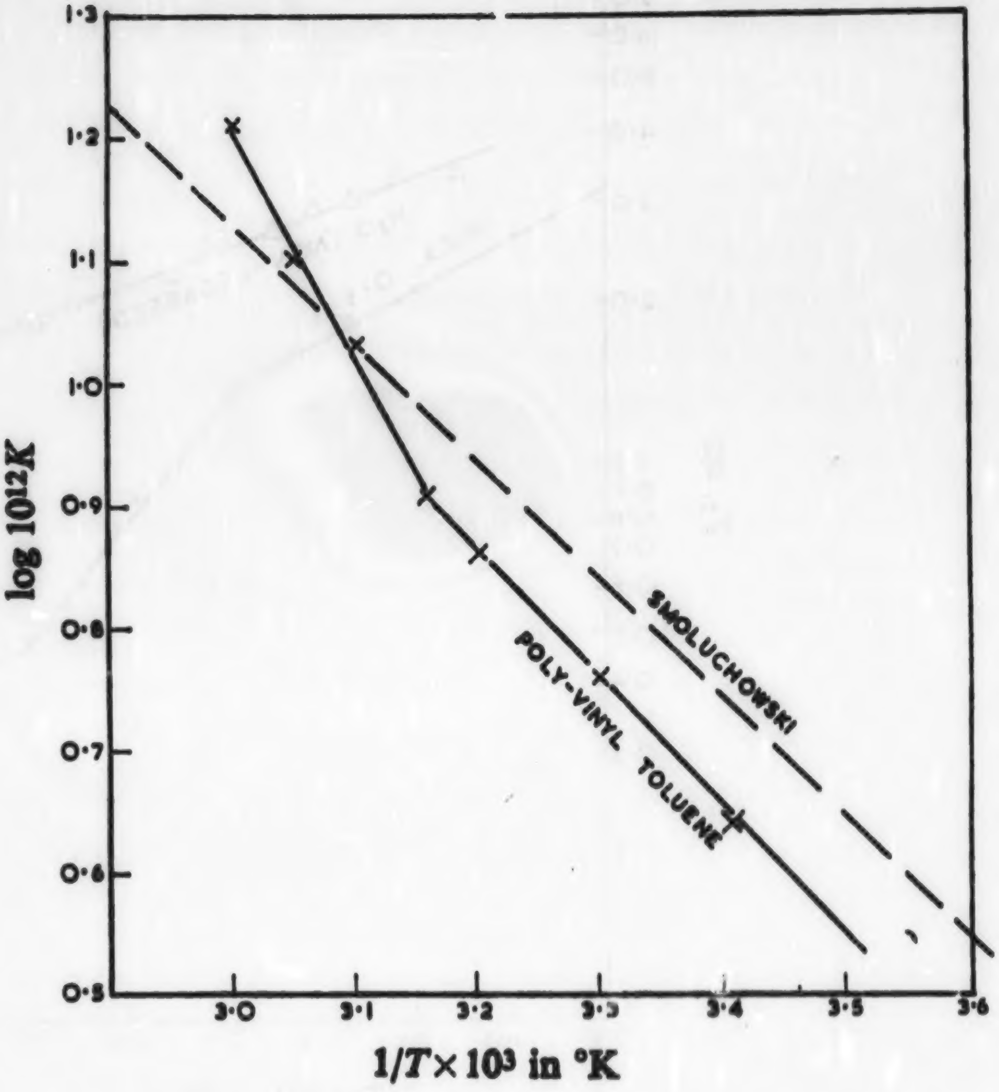
As indicated in the preceding sections, only the most elementary aspects of colloidal stability have yet been elucidated theoretically. The expressions available for determining colloidal stability usually contain in the rate expressions reference to the linear or exponential temperature dependencies. However, as stressed before, most theoretical predictions would indicate relatively simple and certainly "smooth" temperature-dependent behavior. The complexity of the problem, however, for actual systems, can be seen quite readily from the simple case discussed by Lewin (1960). The major problem is the formation of many types of non-stable states which may be formed. Thus, for simple reactions leading to an insoluble product, a "full accounting" of possible temperature effects would involve kinetic rate expressions for each of the many consecutive and/or simultaneous reactions - each no doubt with differing enthalpies and entropies of activation. For this reason, theoretical predictions of the kinetics of precipitation of insoluble products generally cannot be expected to yield reliable results - nor can rates of solution be predicted theoretically. In addition to the complexity indicated in Figure I-26, one need most likely also include distinct differences in the role played by the water of hydration for each of the metastable states indicated.

In practical terms, assessments of expected changes in equilibrium properties in composition of natural water systems may be obtained by the approach discussed in Sections II,III of this review. However, the rate with which these changes will be effected may become highly tmeperature-dependent wherever aqueous, interfacial processes are involved, particularly those involving the solid/water interface such as a mineral grain/water interface, or the interface between a dispersed organic material or a cellular organism and the water.

In this section, we review some unexpected anomalous temperature effects on colloidal phenomena to illustrate the points discussed above. It will become obvious that few generalizations can be made, but that caution must be urged in predicting the effects of ambient temperature changes on the overall composition of natural waters involving colloidal phenomena.

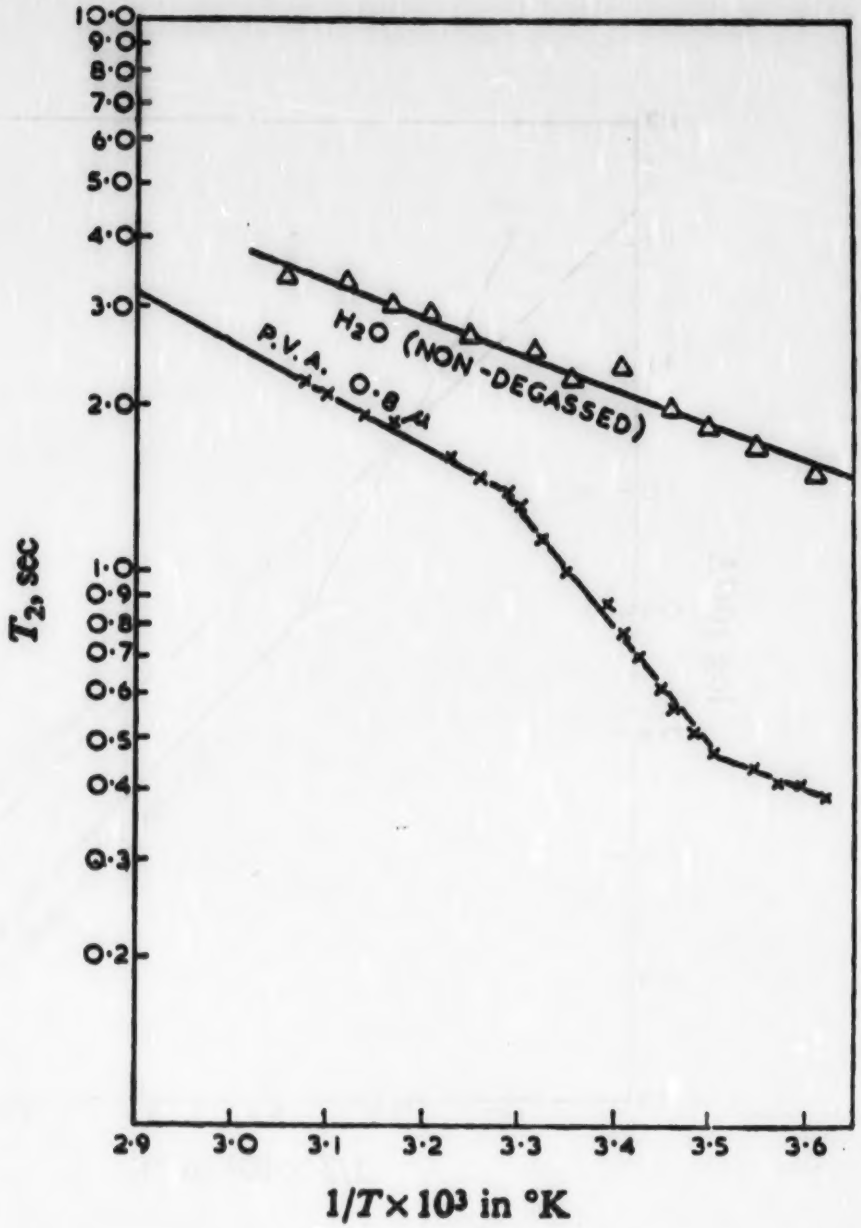
Thermal Anomalies.

It appears that water near interfaces may undergo extensive restructuring. Some of the evidence for this restructuring is manifested in the abrupt changes in the properties of water near interfaces, referred to earlier. In connection with the problem of colloidal stability, only two examples will be mentioned. Johnson et al (1966) have studied the role of water structure in determining colloidal stability; specifically, they measured the dependence of the absolute rate of flocculation (K) of polyvinyl toluene particles on temperature. Their results are shown in the form of an Arrhenius graph in Figure 1-29. A sharp change in slope is observed, indicating an abrupt change in slope, which is likely due to a transition from one type of vicinal water structure to another. The same authors also measured the spin-spin relaxation time (T_2) as a function of temperature for polyvinyl alcohol particles (average 0.8 micron diameters). The results are shown in Figure 1-30. Again, sharp changes in slope are observed. Additional examples of rather abrupt changes with temperature in the properties of vicinal water are shown in Part 2 of this review (Section II-B; Figure 2-10; 2-11; and 2-12). For a detailed discussion of various aspects of water structure near solid surfaces, the reader is referred specifically to an article by Drost-Hansen (1969).



Log flocculation rate (K 10^{12}) as function of 1/T for PVT particles (Johnson et. al., 1966).

Fig. I - 29



Spin - spin relaxation rate as function of I/T for 0.8 PVA particles (and for dehassed water) (Johnson et al., 1966)

Figure I -30

B. Colloid Stability

Stumm and Morgan have rather concisely reviewed the "conventional wisdom" of colloidal stability. Tables I-64, I-65, and Figure I-27 from the monograph by Stumm and Morgan, show some of the equations for the more important physical aspects of colloidal systems.

At this time, attention is called particularly to the fact that the "classically derived" expressions for colloidal properties all contain or allow for temperature variations via temperature itself as a prefactor (T or T^{-1}) or as exponential (such as, for instance, the expression for the surface potential, as given by Equation 12-a, Table I-64, where κ is the reciprocal thickness of the electric double layer (cm^{-1}). Typically, no abrupt, sudden changes are to be expected in the properties of colloid suspensions, as a function of temperature from this general type of theoretical treatment. Yet, many colloidal phenomena show unusual temperature dependencies, particularly in rate expressions.

Table I-64

Gouy–Chapman Theory of Single Flat Double Layer†

I. VARIATION OF CHARGE DENSITY IN SOLUTION

Equality of electrochemical potential, $\bar{\mu}$ $(= \mu + zF\Psi)$ of every ion, regardless of position.

Electrochemical Potential

$$\bar{\mu}_{+(x)} = \bar{\mu}_{+(x=\infty)}; \qquad \bar{\mu}_{-(x)} = \bar{\mu}_{-(x=\infty)} \tag{1}$$

$$zF(\Psi_{(x)} - \Psi_{(x=\infty)}) = RT \ln \frac{n_{+(x)}}{n_{+(x=\infty)}} = -RT \ln \frac{n_{-(x)}}{n_{-(x=\infty)}} \tag{2}$$

Cations $\quad n_+ = n_{+(x=\infty)} \exp(-zF\Psi_{(x)}/RT)$ (3)

Anions $\quad n_- = n_{-(x=\infty)} \exp(zF\Psi_{(x)}/RT)$ (4)

Charge Density $\quad q = zF(n_+ - n_-)$ (5)

II. LOCAL CHARGE DENSITY AND LOCAL POTENTIAL

Ψ and q are related by Poisson's equation

Poisson's Equation $\quad d^2\Psi/dx^2 = -(4\pi/\varepsilon)q$ (6)

Combining (3), (4), and (5) with (6) and considering that $\sinh x = (e^x - e^{-x})/2$ gives the *Double-Layer Equation*

$$d^2\Psi/dx^2 = \kappa^2/(zF/RT) \sinh(zF\Psi/RT) \tag{7}$$

where

$$\kappa = \left(\frac{8\pi n e^2 z^2}{\varepsilon kT}\right)^{1/2} = \left[\frac{8\pi e^2}{\varepsilon kT}\left(\frac{NI}{10^3}\right)\right]^{1/2} \tag{8}$$

For convenience the following substitutions can be made:

$$y = zF\Psi/RT; \qquad Z = zF\Psi_0/RT; \qquad \xi = \kappa x \tag{9}$$

Considering (9), (8) becomes

Substituted Double-Layer Equation

$$d^2y/d\xi^2 = \sinh y \tag{10}$$

For boundary conditions, if $\xi = \infty$, $dy/d\xi = 0$ and $y = 0$

first integration: $\quad dy/d\xi = 2\sinh(y/2)$, or (11)

$$d\Psi/dx = \frac{RT}{zF} 2\kappa \sinh(y/2) \tag{11a}$$

and for boundary conditions, if $\xi = 0$, $\Psi = \Psi_0$ or $y = Z$

second integration: $\quad e^{y/2} = \dfrac{e^{Z/2} + 1 + (e^{Z/2} - 1)e^{-\xi}}{e^{Z/2} + 1 - (e^{Z/2} - 1)e^{-\xi}}$ (12)

Simplified Equations for $\Psi_0 < 25$ mV

Instead of (7) $\quad d^2\Psi/dx^2 = \kappa^2\Psi$ (7a)

Instead of (12) $\quad \Psi = \Psi_0 \exp(-\kappa x)$ (12a)

III. TOTAL DOUBLE-LAYER CHARGE AND Ψ_0

Total Charge: $\quad \sigma = -\int_0^\infty q\,dx = \varepsilon/4\pi \int_0^\infty (d^2\Psi/dx^2)dx$

$$= -\varepsilon/4\pi[d\Psi/dx]_{x=0} \tag{13}$$

Gouy-Chapman theory of a single, flat electrical double layer (from Stumm and Morgan, 1970, page 460).

Table I-64 Continued

Inserting (11*a*):

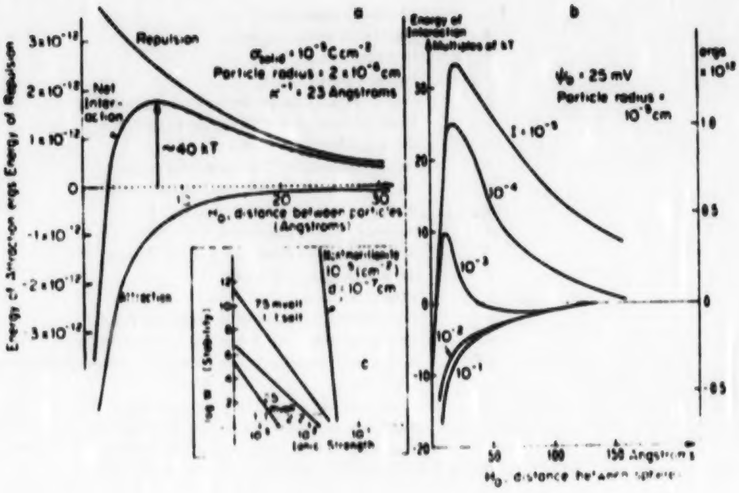
$$\sigma = [(2/\pi)\epsilon kT\bar{n}]^{1/2} \sinh (zF\Psi_0/2RT) \qquad (14)$$

Simplified equation for small Ψ_0:

$$\sigma \simeq (\epsilon\kappa/4\pi)\Psi_0 \qquad (14a)$$

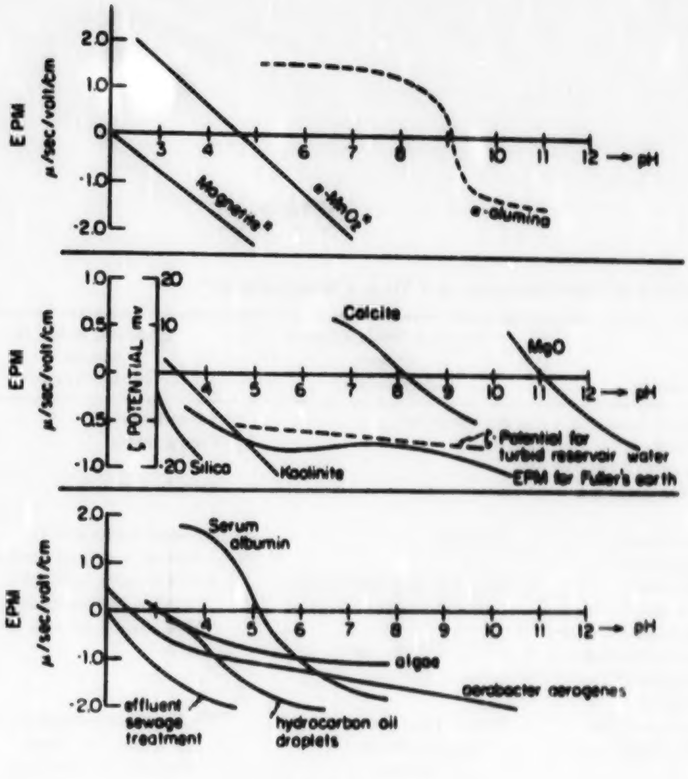
---

† μ	chemical potential
$\bar{\mu}$	electrochemical potential
Ψ	local potential, V
Ψ_0	surface potential, V
q	(volumetric) charge density, coulombs cm^{-3}
σ	total surface charge, coulombs cm^{-2}
x	distance from surface, cm
n_+	local cation concentration, moles cm^{-3}
n_-	local anion concentration, moles cm^{-3}
$n_{(x=\infty)}$	bulk ion concentration, moles cm^{-3}
$\bar{n}$	number of ion pairs, cm^{-3} ($= Nn_{x=\infty}$)
N	Avogadro's number, 6.03×10^{23} mole^{-1}
I	ionic strength, mole liter^{-1}
z	valence of ion
κ	reciprocal thickness of double layer, cm^{-1}
e	charge of electron, 1.6×10^{-19} coulombs
kT	Boltzmann constant times absolute temperature, 0.41×10^{-20} V coulomb at 20 C
$RT = N \times kT = 2.46 \times 10^3$, V coulomb mole^{-1}	
ϵ	dielectric constant, 89×10^{-12} coulombs V^{-1} cm^{-1}
F	Faraday $= 6 \times 10^{23} \times e$, coulombs equiv^{-1} = 96,500 coulombs equiv^{-1}
$F\Psi/RT = e\Psi/kT = 1$ for $\Psi = 25$ mV at 20 C	



Energetics aspects of classical theory of colloidal stability (Stumm and Morgan, 1970, page 497).

Figure 1-27



pH dependence of charge on various suspended materials. The data are of only semi-quantitatively significance. However, the data do indicate some degree of parallelism between the colloidal properties of purely inorganic colloids in natural waters and organic or living material (bacteria and algae). (Stumm and Morgan, 1970, p. 455).

Figure 1-28

Table 1-65

Modes of Destabilization and Their Characteristics†

Phenomena	Physical Double-Layer Theory (Coagulation)	Chemical Bridging Model (Flocculation)	Aggregation by Adsorbable Species (Adsorption Coagulation)‡
Electrostatic interaction	Predominant	Subordinate	Important
Chemical interactions, and adsorption	Absent	Predominant	Important
Zeta potential for optimum aggregation	Near zero	Usually not zero	Not necessarily zero
Addition of an excess of destabilizing species	No effect	Restabilization due to complete surface coverage	Restabilization usually accompanied by charge reversal
Relationship between optimum dosage of destabilizing species and the concentration of colloid (or concentration of colloidal surface)	CCC virtually independent of colloid concentration	Stoichiometry, a linear relationship between flocculant dose and surface area	Stoichiometry possible but does not always occur
Physical properties of the aggregates which are produced	Dense, great shear strength but poor filtrability in cake filtration	Flocs of 3-dimensional structure; low shear strength but excellent filtrability in cake filtration	Flocs of widely varying shear strength and density

† From W. Stumm and C. R. O'Melia, *J. Amer. Water Works Assoc.*, 60, 514 (1968).

‡ Aggregation by hydrolyzed metal ions fits into this category.

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Various aspects of stabilization of aqueous colloidal systems.

(Stumm and Morgan, 1970, page 501).

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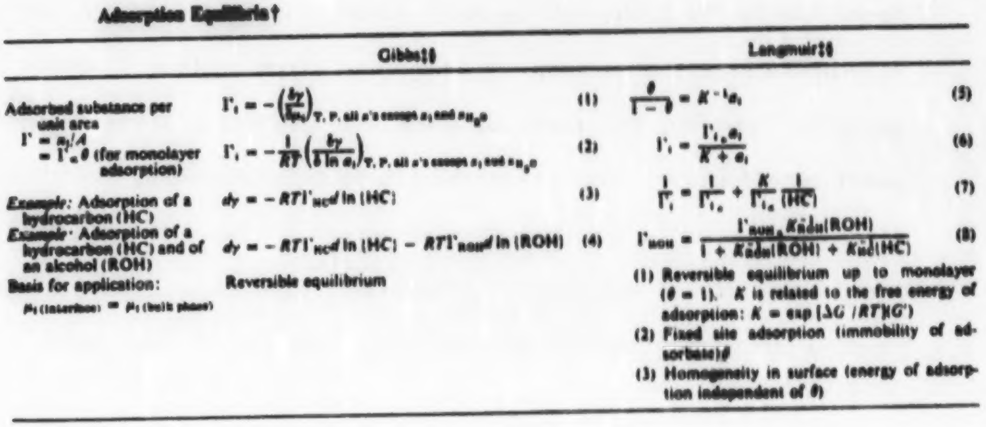
C. Adsorption-Desorption Phenomena

Various adsorption processes play a crucial role in determining the overall chemical properties of natural waters. The classical expressions for estimating adsorption equilibria are shown in Table I-66, from the monograph by Stumm and Morgan (1970). The Table shows the "conventional wisdom" with regard to adsorption.phenomena, specifically the Gibbs and Langmuir adsorption isotherms. A vast literature exists on adsorption phenomena (from aqueous solutions) in general. However, far fewer data are available specifically on temperature effects on adsorption equilibria. Furthermore, the complications introduced in the preceding paragraph - namely those due to the possibility of different vicinal water structures - must be kept in mind in connection with all adsorption-desorption phenomena.

Table I-66



Adsorption Equilibria†

	Gibbs‡§		Langmuir‡§	
Adsorbed substance per unit area	$\Gamma_i = -\left(\frac{\partial\gamma}{\partial\mu_i}\right)_{T,\,P,\,\text{all } a\text{'s except } a_i \text{ and } a_{H_2O}}$	(1)	$\frac{\theta}{1-\theta} = K^{-1}a_i$	(5)
$\Gamma = n_i/A$ $= \Gamma_m\theta$ (for monolayer adsorption)	$\Gamma_i = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial\ln a_i}\right)_{T,\,P,\,\text{all } a\text{'s except } a_i \text{ and } a_{H_2O}}$	(2)	$\Gamma_i = \frac{\Gamma_{i_m}a_i}{K+a_i}$	(6)
Example: Adsorption of a hydrocarbon (HC)	$d\gamma = -RT\Gamma_{HC}\,d\ln(HC)$	(3)	$\frac{1}{\Gamma_i} = \frac{1}{\Gamma_{i_m}} + \frac{K}{\Gamma_{i_m}}\frac{1}{(HC)}$	(7)
Example: Adsorption of a hydrocarbon (HC) and of an alcohol (ROH)	$d\gamma = -RT\Gamma_{HC}\,d\ln(HC) - RT\Gamma_{ROH}\,d\ln(ROH)$	(4)	$\Gamma_{ROH} = \frac{\Gamma_{ROH_m}K_{ROH}^{ads}(ROH)}{1 + K_{ROH}^{ads}(ROH) + K_{HC}^{ads}(HC)}$	(8)
Basis for application: $\mu_{i\,(\text{interface})} = \mu_{i\,(\text{bulk phase})}$	Reversible equilibrium		(1) Reversible equilibrium up to monolayer ($\theta = 1$). K is related to the free energy of adsorption: $K = \exp[\Delta G/RT](G^\circ)$ (2) Fixed site adsorption (immobility of adsorbate)¶ (3) Homogeneity in surface (energy of adsorption independent of θ)	

Classical adsorption equilibria. (Stumm and Morgan, 1970, page 452).

(For an explanation of symbols, see next page).

Table 1-66 Continued

† μ = chemical potential
γ = interfacial tension, erg cm^{-2}
a_i = activity of species *i*, *M*
θ = fraction of surface covered with adsorbate
R = gas constant
K = adsorption equilibrium constant, *M* (if $K = a_i$, $\theta = 0.5$)
Γ_i = adsorption density, moles cm^{-2}

‡ In most cases, concentrations may be used instead of activities; however, the bulk concentration can no longer be defined in terms of quantities added if the solutes have associated to form micelles. Similar difficulties arise when the adsorbates in the interface undergo irreversible changes, such as denaturation reactions.

§ Γ_i is defined in such a way that in dividing the interface, the adsorption density of water is zero (Gibbs convention).

A similar adsorption model for multilayer adsorption has been set forth in the *Brunauer, Emmett and Teller* (*BET*) equation which has the form:

$$X = \frac{X_m B a_i}{(a_{is} - a_i)[1 + (B - 1)a_i/a_{is}]}$$

where X and X_m are the observed and ultimate quantity of substance adsorbed per unit area, B, an energy related constant, and a_{is} is the saturation activity of the solute.

ε Varying energies of adsorption can arise because of heterogeneity of the surface, that is, the free energy decreased with coverage. The Tempkin isotherm is based on such a model. In the *Tempkin isotherm*, θ is a function of log a_i at intermediate coverages ($0.2 < \theta < 0.8$).

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